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DEPARTMENT OF METALLURGY
AND MATERIALS SCIENCE

Final Report

of the Project on

CHEMICAL REACTIVITY

OF METALLURGICAL COKE

by

W-K. Lu
McMaster University

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to be submitted to

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1. SUMMARY

A. Objectives

Chemical reactivity of commercial and laboratory cokes with respect to carbon dioxide in gases is the subject of this investigation. The catalytic effect of potassium and the effect of specific surface (and indirectly carbonization conditions and coal blends) are the major topics of this study. The monitoring of weight changes due to chemical reactions, electron microscopy for structures and optical microscopy for texture, were proposed as the appropriate techniques for this project.

B. Achievements

Commercial cokes and laboratory cokes provided by CANMET were used in this investigation. It has been found that chemical reactivity of cokes depends on specific surface area of coke (and indirectly on carbonization temperature and coal blends). However, the "catalytic effect" of potassium overshadows all the factors mentioned above. The mechanism of the so-called "catalytic effect" involves the disruption of coke structure due to the formation of microporosity and microcracks. The addition of hydrogen to the standard oxidizing gas resulted in lower thermodynamic oxidizing power of the gas, but surprisingly, sped up the rate of oxidation of carbon in coke. This is of very important consequence in the blast furnace.

2. COKE SAMPLES

There were two types of coke samples, i.e., commercial and laboratory cokes, used in this project.

A. Commercial Cokes

A1-1, A1-2, and A1-3 were made from the same coal blend but there was a difference in the final temperature reached. It has been found in the present

work that the lower the peak carbonization temperature, with little variation in coking time, the more reactive the coke was, with respect to CO_2 oxidation.

S-A, S-B and S-C were made by one steel company. S-A was the typical product and S-C was made during a strike (very long coking time with lower flue temperature) from the same coal blend. S-B was made in a new tall oven with minor changes in coal blend in comparison with S-A and S-C.

S1, S2, S3, S4, S5, S6, S7 and S8 were made in a series of trials in which the total amounts of low volatile coals (26%) and high volatile coals (74%) remained constant, with varying amounts from individual mines. These eight cokes may be divided into two sub-groups based on the battery of ovens from which these cokes were made. They are (S2, S7, S8 and S4) and (S6, S3, S1 and S5).

Re coke is a single coal coke made by a U.S. steel company.

B. Laboratory Cokes Supplied by CANMET

Among the ten samples supplied by CANMET, seven were made in their laboratory oven under better controlled conditions and three were commercial cokes (1001, 1002 and 1004) which were included for comparison. Coke samples 654, 662 and 670 were made from single coals. With the additon of 7% pitch of particular properties to these coals, the resultant cokes were labelled 656, 664 and 672, respectively. Samples 672 and 678 are different only in properties of additives.

3. SEM OBSERVATIONS: TWO TYPES OF SURFACES

SEM micrographs of cokes are presented in 24 figures which may be classified in the following categories, i.e.,:

(A) As-received (Figs. 1 to 3).

(B) After potassium impregnation in Ar-K gaseous mixture (Figs. 4 and 5).

(C) After oxidation $N_2/CO_2/CO$ mixture (Figs. 6 to 11).

(D) After potassium impregnation, then, followed by oxidation (Figs. 12 and 13).

(E) After potassium impregnation, moisture absorption, moisture absorption and soaking in water (Figs. 14 to 21).

(F) Other interesting features (Figs. 22 to 24).

(A) In Figs. 1 to 3, the micrographs of cokes Re-1, Al-1 and Al-3 are given. They demonstrate that in general the fracture surface (by breaking pore walls) and the internal surface of pores are different. Up to the magnification (shown on each photograph) of 5000x, one may conclude that the fracture surface is relatively rougher and more permeable for gas diffusion. The sharper edges may indicate that carbon on the fracture surface may be energetically more favourable for chemical reactions.

(B) In Figs. 4 and 5, the changes which may be observable by SEM, as the result of potassium absorption are examined. New phases which grew outward from the original surface and the formation of fine cracks are certain. Whether the fine pores under the new phases is the cause or the consequence of their growth is unknown.

(C) The fact that the pore surface appears to be more resistant to oxidation is given in Figs. 6 to 11. The highly selective oxidation of Al-1 specimen is shown in Figs. 10 and 11.

(D) The so-called "catalytic" effect of alkalies in carbon oxidation is examined in Figs. 12 and 13. Comparing with cases shown in Figs. 6 to 11, these oxidation experiments were carried out at lower temperature (850° instead of 950°C) and for shorter time. Potassium makes both types of surfaces more reative to the extent that the difference in reactivity between them is no longer significant.

(E) The new phases which formed as the result of potassium impregnation (see Figs. 4 and 5) have been determined qualitatively in SEM to be potassium-rich. However, it is not possible based on information available at the present time to identify the chemical nature of these phases. They might be intercalation compounds, carbonates, hydroxides, etc. The series of moisture absorption and soaking experiments were developed. Micrographs of these specimens are given in Figs. 14 to 21. The success in the removal of new phases varies. The best are shown in Figs. 17 and 20. The damages in the carbon structures are visible in all cases. However, the damages in the formation of cracks and fine pores, in principle, can occur either at 1000°C during potassium impregnation or at room temperature during the extraction of potassium from carbon structure by oxidation reactions. Work on the study of the mechanisms will continue.

(F) The beautiful mesophase present in some Re-1 cokes is shown in Fig. 22. In the same figure, sheets of solids (presumably carbonaceous) remain in a specimen which suffered a high degree of burn-off. It could be that these sheets were the skin of the internal surface of pores. Obviously, for unknown reasons, they are resistant to oxidation. In Fig. 23, photographs 1, 3 and 5 may be examined with Figs. 10 and 11. These photographs could represent the structure leading to that in Fig. 11 after partial oxidation. For similar reasons, photographs 2, 4 and 6 could be related to that in Fig. 10. The fibrous substances shown in Fig. 24 are interesting but we cannot be sure they are carbonaceous.

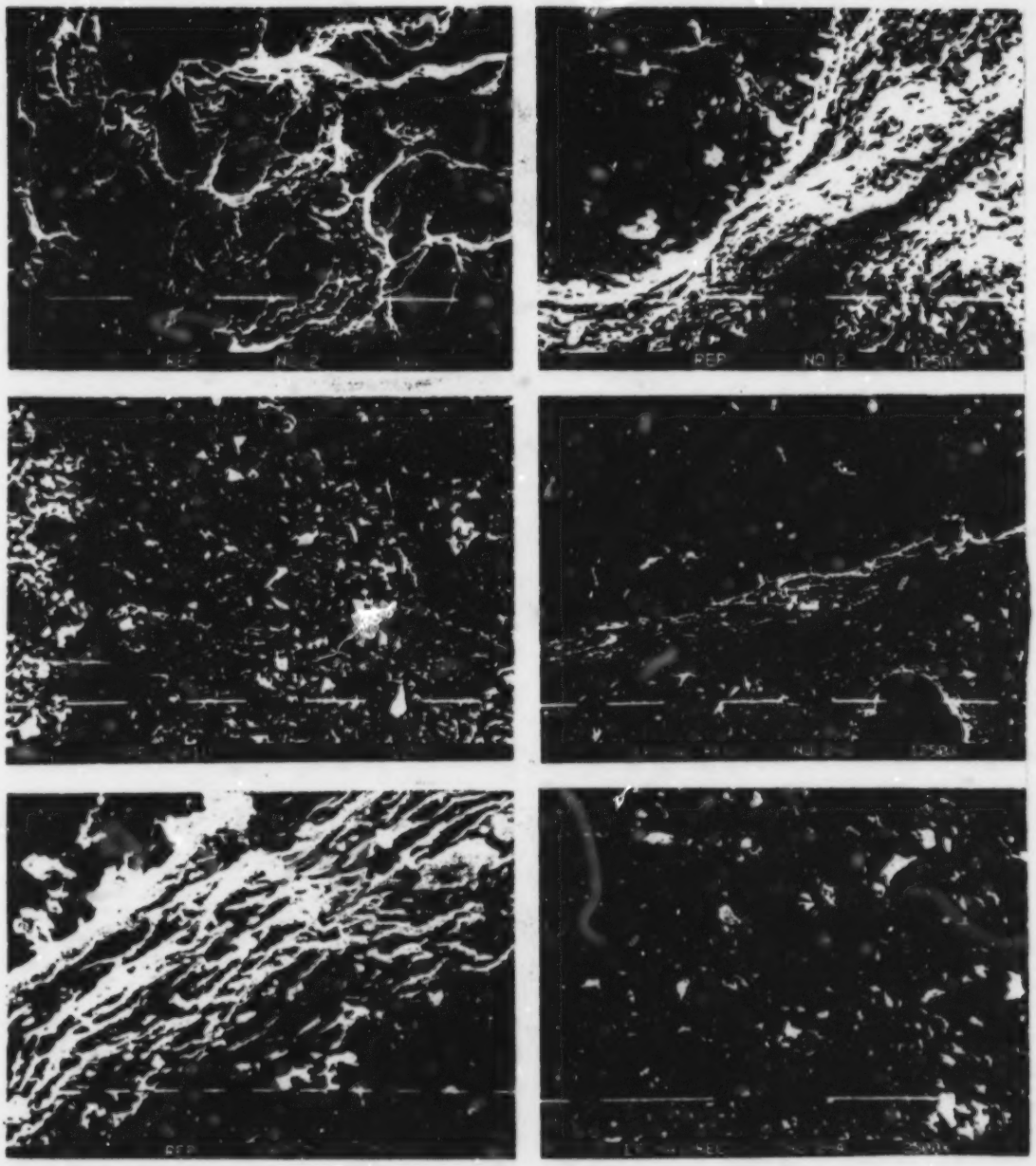


Fig. 1 SEM micrographs of Re-1 coke as-received.

1	2
3	4
5	6

Photographs 1 & 2: Overall view of two types of surfaces.

Photographs 3 & 5: Fracture surfaces.

Photographs 4 & 6: Pore surfaces.

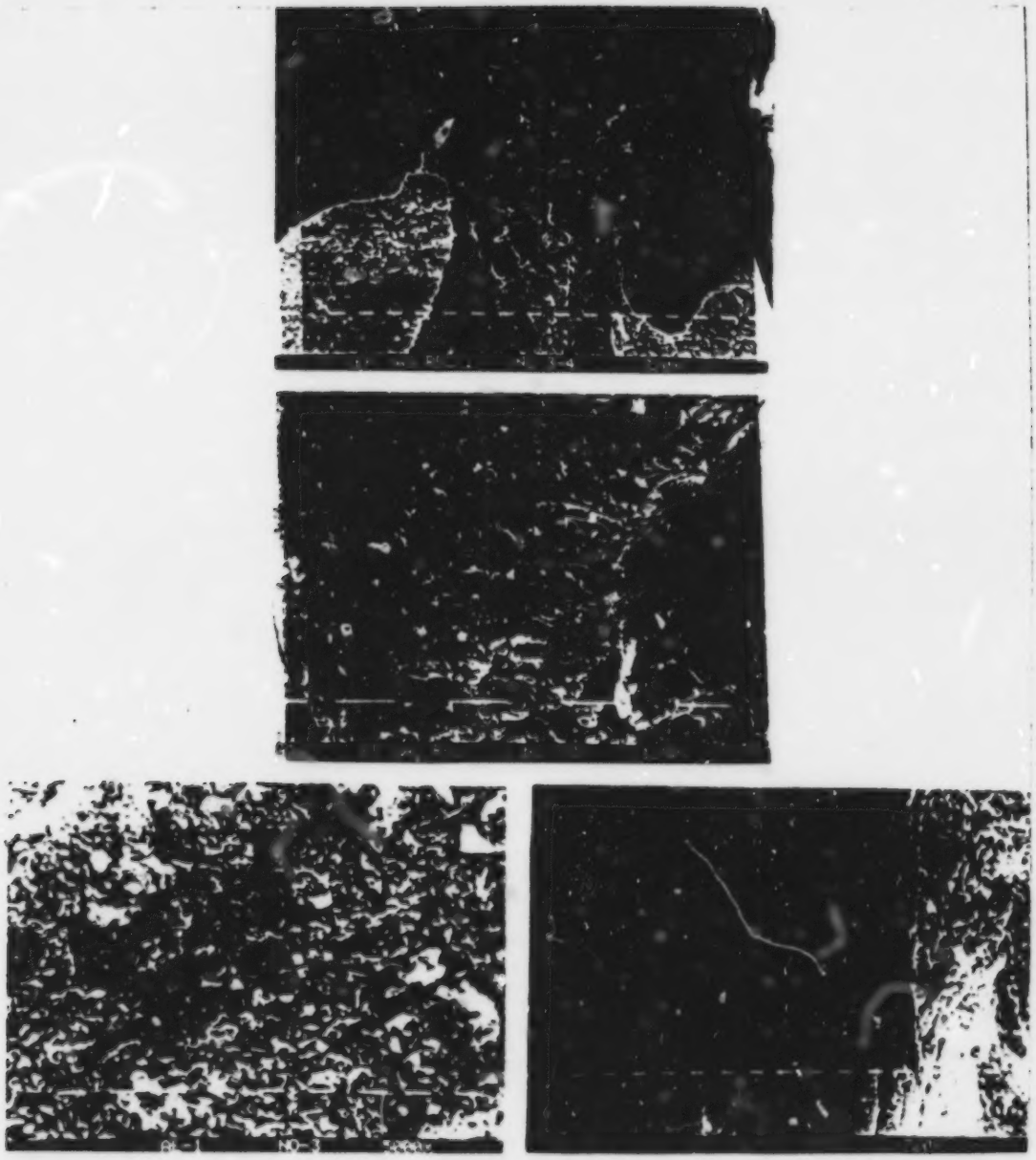
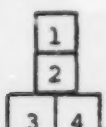


Fig. 2 SEM micrographs of Al-1 coke as-received.



Photographs 1, 2 and 4: Typical fracture and pore surfaces.

Photograph 3: Highly magnified fracture surface.

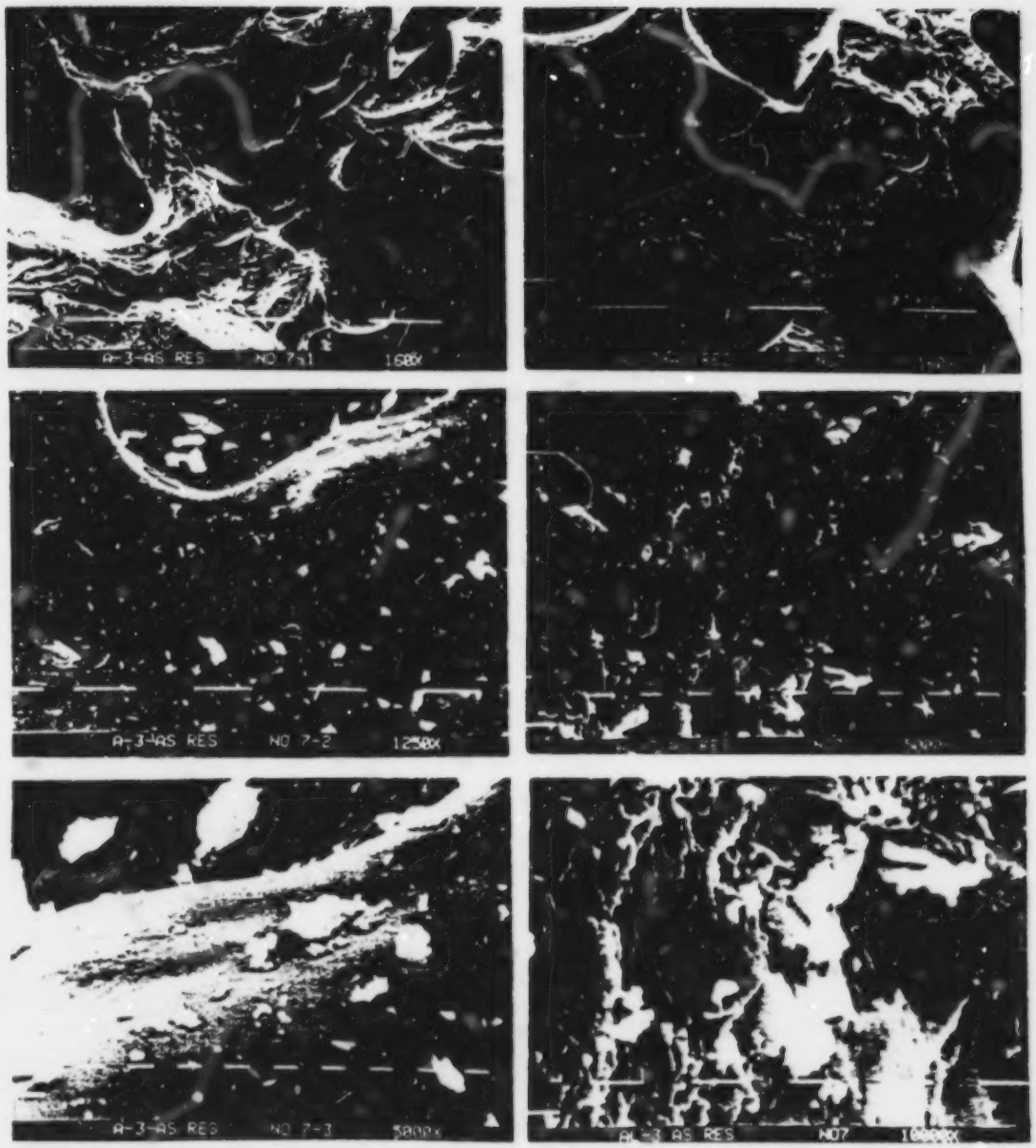


Fig. 3 SEM micrographs of A1-3 coke as-received.

1	2
3	4
5	6

Photographs 1 & 2: Overall view of two types of surfaces.

Photographs 3 & 5: Pore surfaces.

Photographs 4 & 6: Fracture surfaces.

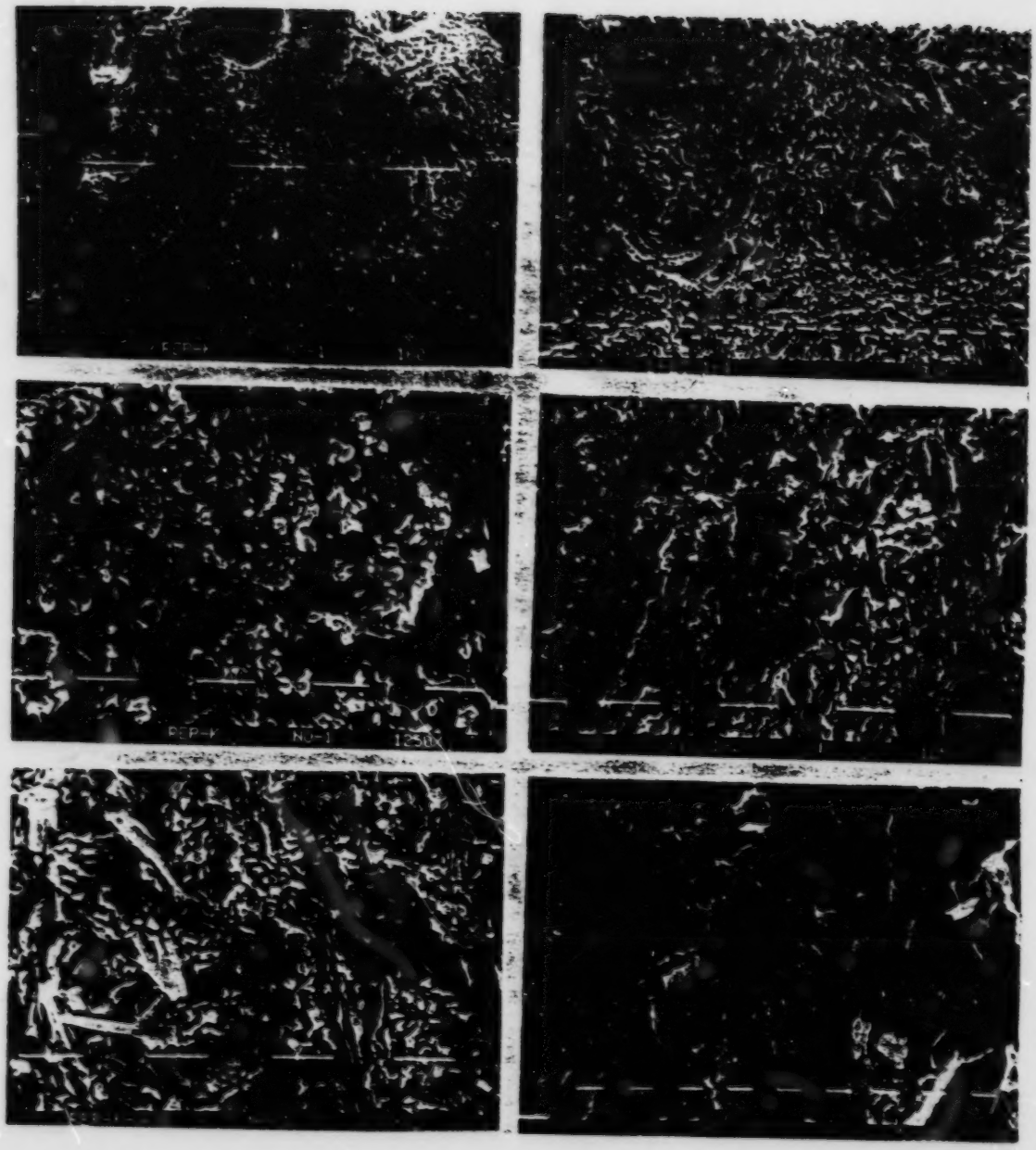


Fig. 4 SEM micrographs of Re-1 coke after K impregnation in Argon-1% potassium vapour at 1000°C and resulting in 3.65 % wt. K in the specimen.

1	2
3	4
5	6

Photographs 1 & 2: Overall view showing formation of new phases on original surfaces.

Photographs 3 to 6: Magnified pictures of new phases.

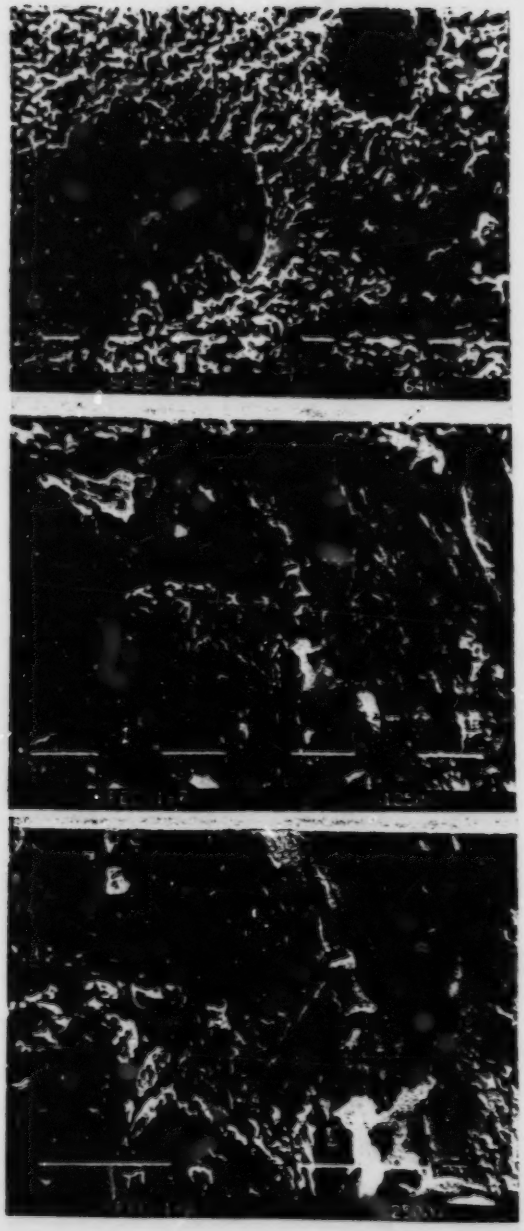


Fig. 5 SEM micrographs of specimens similarly treated as in Fig. 4.

1	Photograph 1: Regions on the surface heavily and lightly covered by the new phases.
2	
3	Photographs 2 & 3: Cracks visible on the sparsely covered surface.

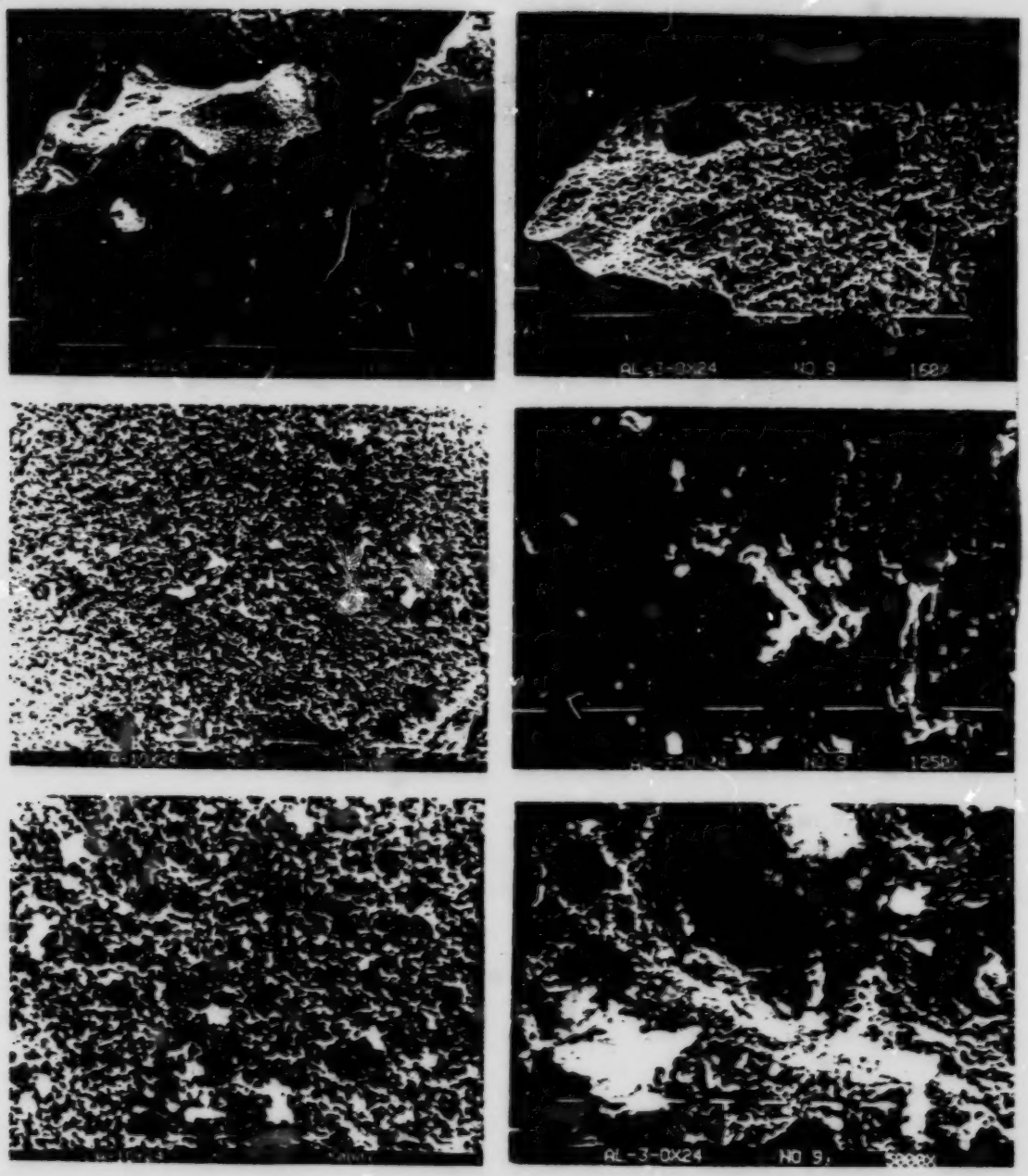


Fig. 6 SEM micrographs of Al-3 coke with 24% burn-off, oxidized at 950°C for three hours.

1	2
3	4
5	6

Photographs 1 & 2: Partially oxidized fracture and pore surfaces.

Photographs 3 & 5: Magnified fracture surfaces.

Photographs 4 & 6: Pore surface appears to be less reactive than fracture surface.

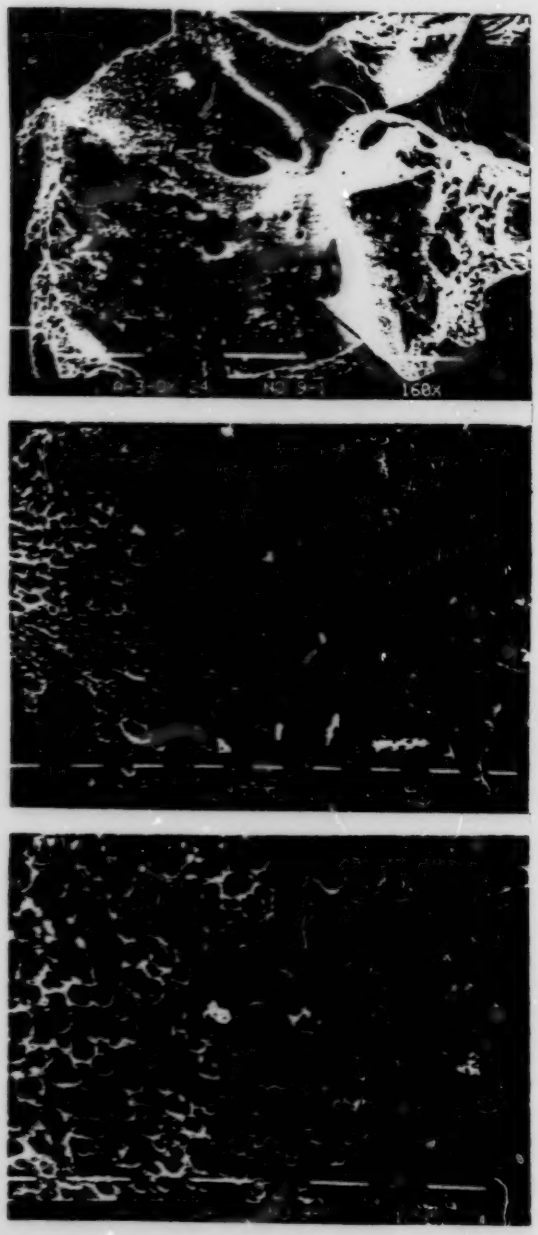


Fig. 7 SEM micrographs of specimens similarly treated as in Fig. 6.

Pitting of the pore surface as the result of oxidation.

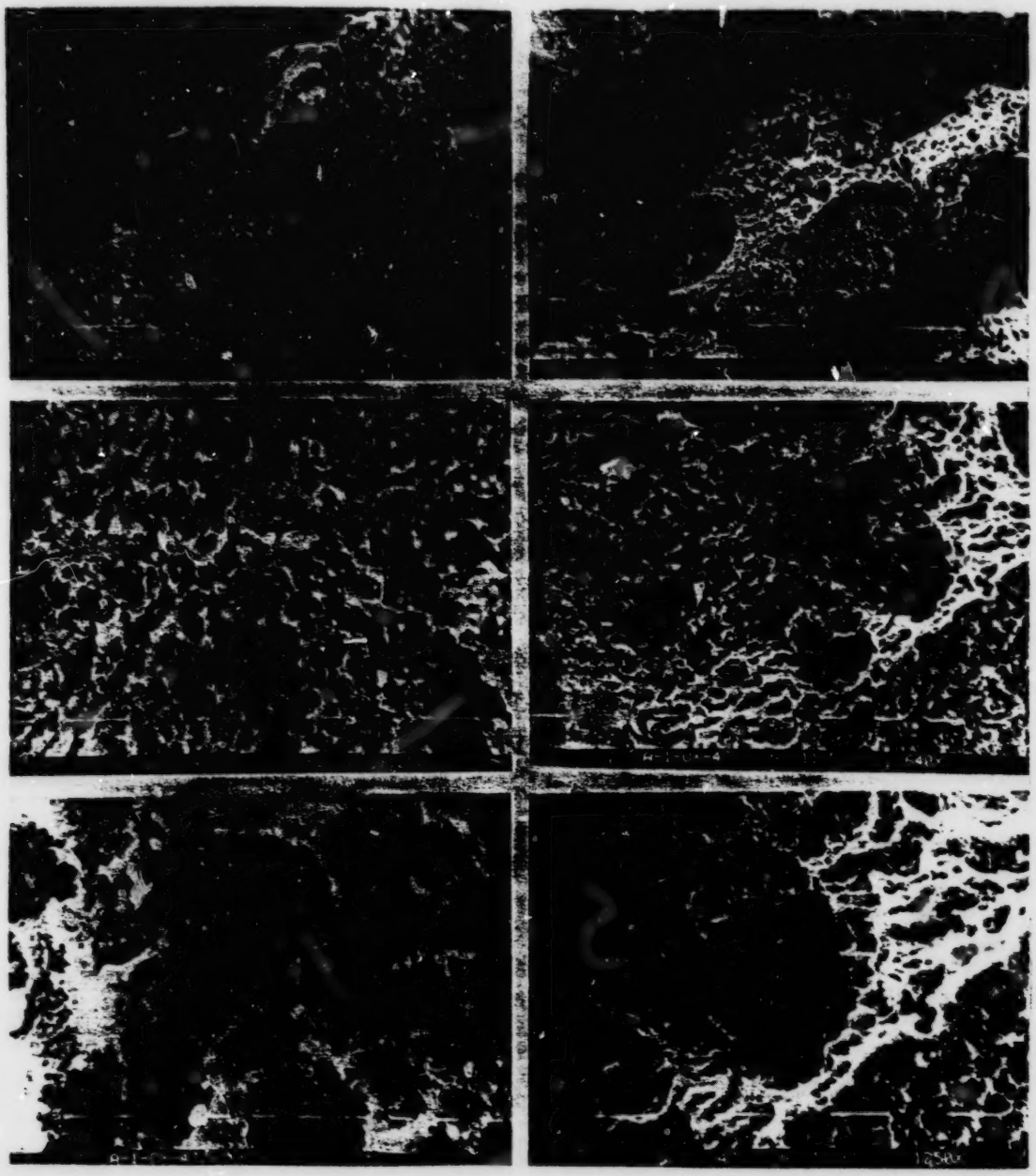


Fig. 8 SEM micrographs of A1-3 coke with 47% burn-off, oxidized at 950°C for nine hours.

1	2
3	4
5	6

Photographs 1 & 2: Oxidation on fracture surfaces appear to be more advanced than on pore surface.

Photographs 3 & 5: Magnified fracture surfaces.

Photographs 4 & 6: Magnified both types of surfaces.

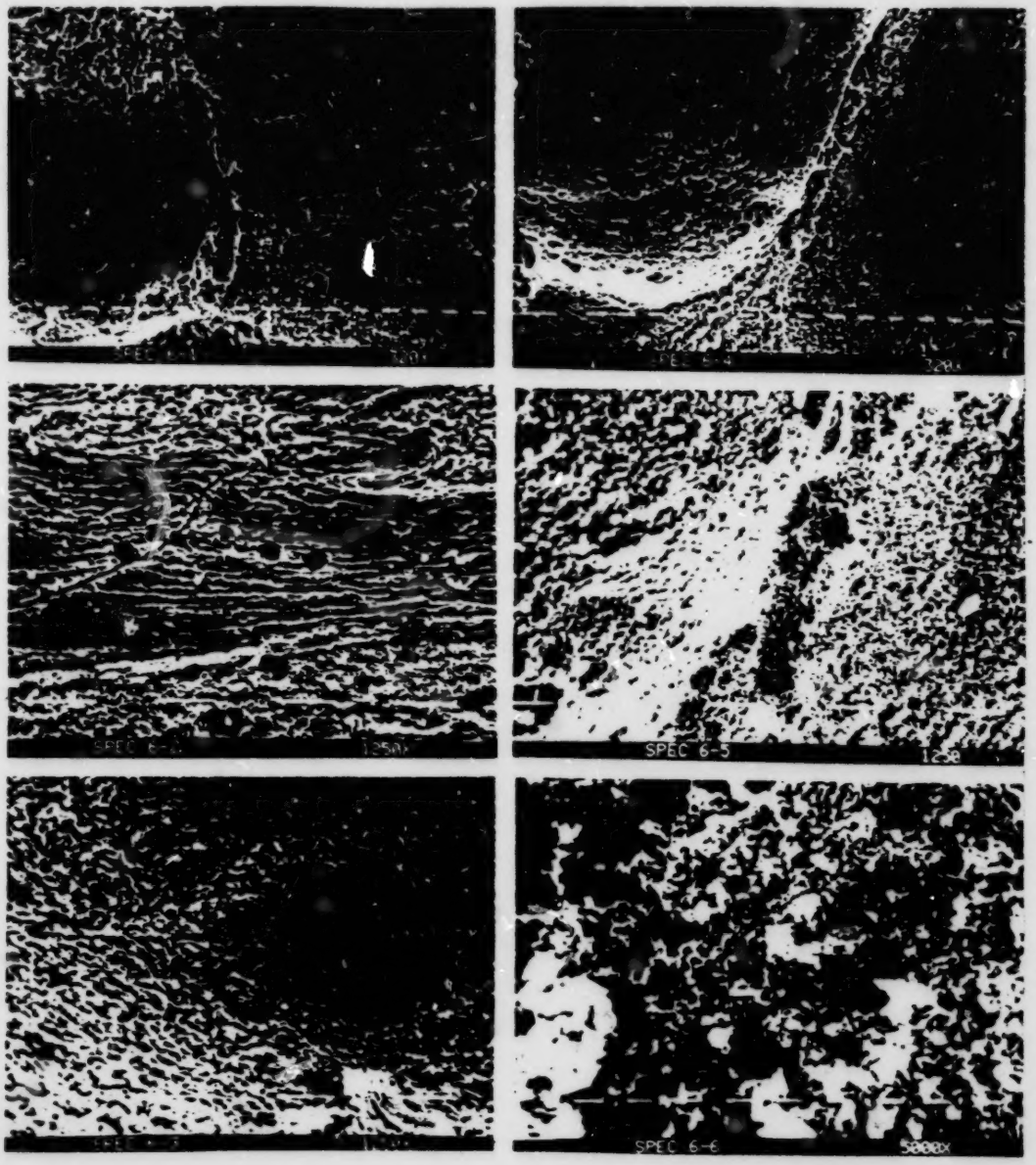


Fig. 9 SEM micrographs of S-B coke with 22.5% burn-off, oxidized at 950°C for four hours.

1	2
3	4
5	6

Photographs 1 & 2: Fracture and pore surfaces.

Photographs 3 & 5: Relatively less reacted pore surfaces.

Photographs 4 & 6: More reacted fracture surfaces.

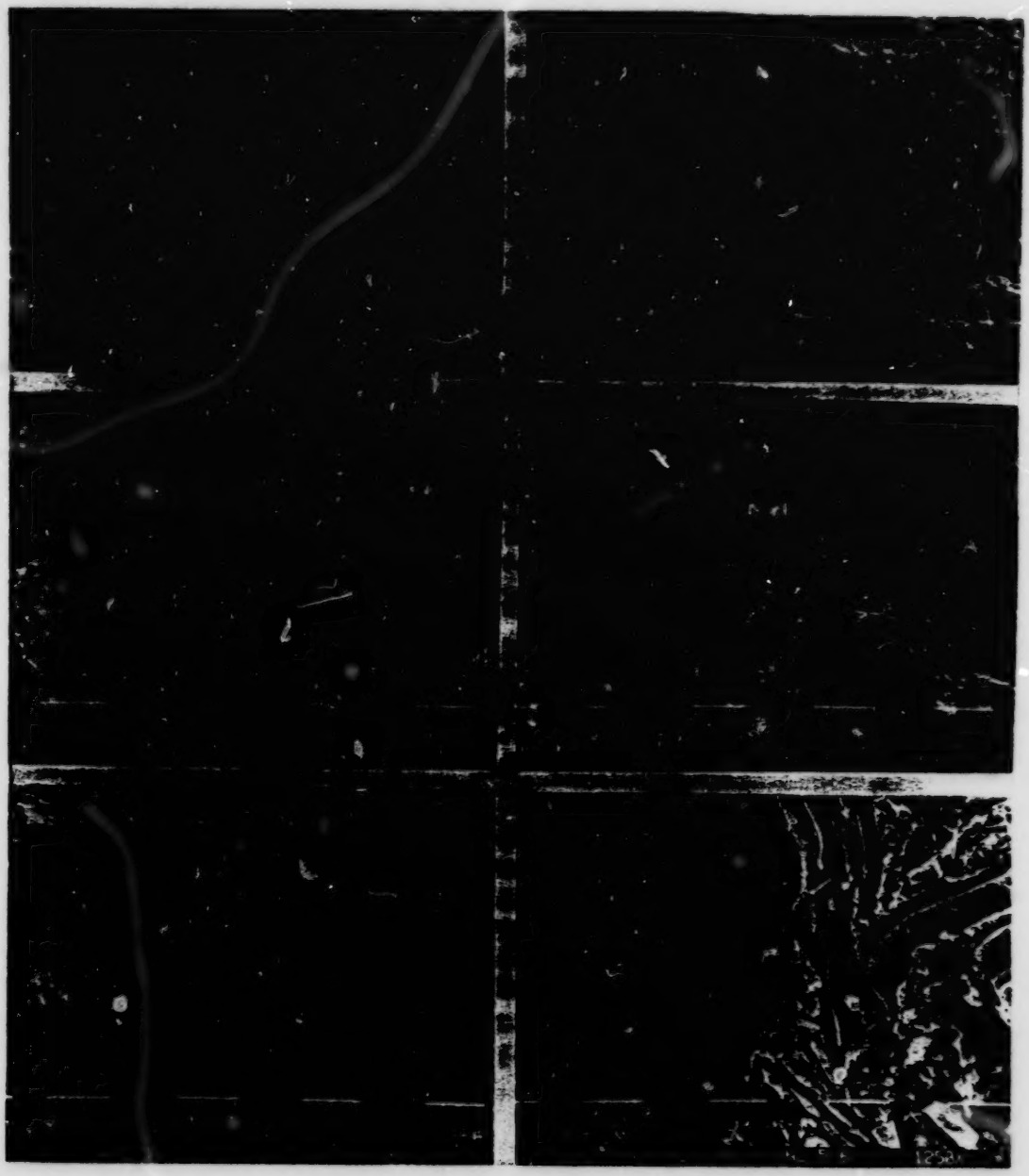


Fig. 10 SEM micrographs of Al-1 coke with 13% burn-off, oxidized at 950°C for four hours.

1	2
3	4
5	6

Photographs 1 & 2: Overall view of pore and fracture surfaces.

Photographs 3 & 5: Fracture surface with certain selective oxidation.

Photographs 4 & 6: Pore surfaces are less reactive. Oxidation is highly selective on fracture surface.

Fig. 11 SEM micrographs of specimens similarly treated as in Fig. 10.

Highly selective oxidation of carbon on fracture surfaces.

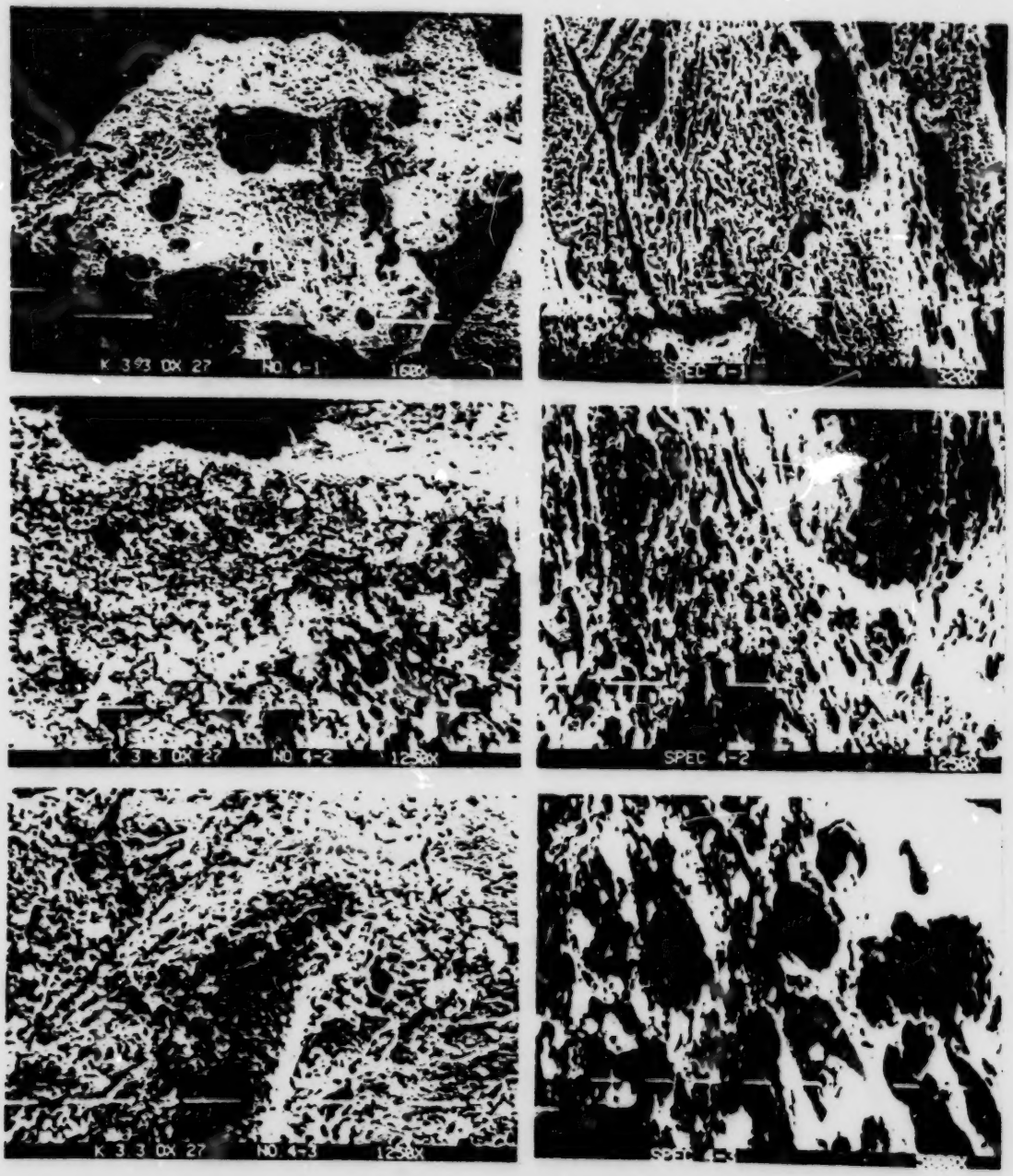


Fig. 12 SEM micrographs of Al-1 coke oxidized (27% burn-off, at 850°C for 1.5 hours) after potassium impregnation (3.3% wt. K).

1	2
3	4
5	6

Photograph 1: Twc types of surfaces.

Photographs 2 & 4: Two types of surface appear to be of comparable reactivity.

Photographs 3, 5 & 6: Fracture surfaces.

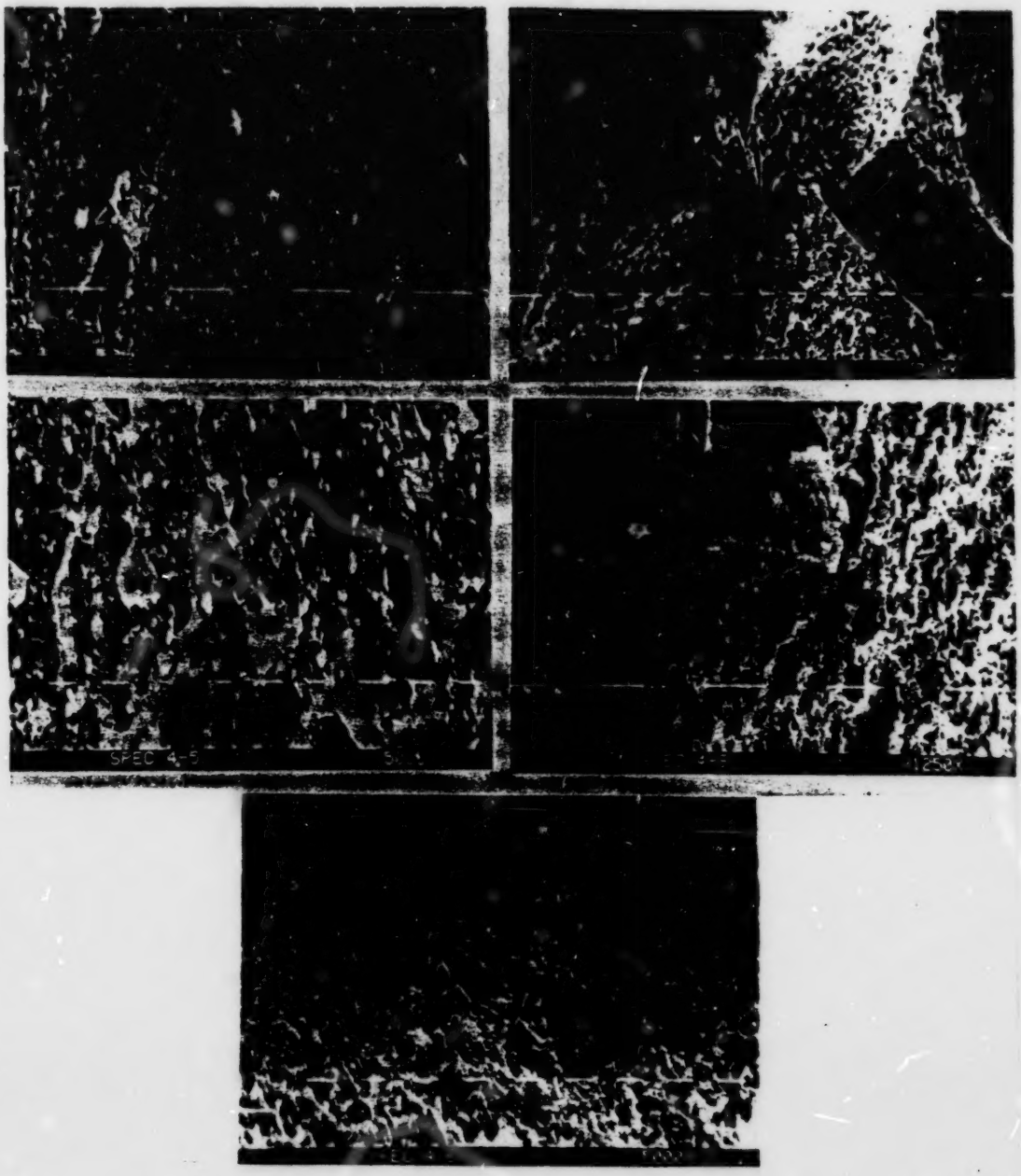


Fig. 13 SEM micrographs of specimens similarly treated as in Fig. 12.

Photographs show comparable reactivity of fracture and pore surfaces.

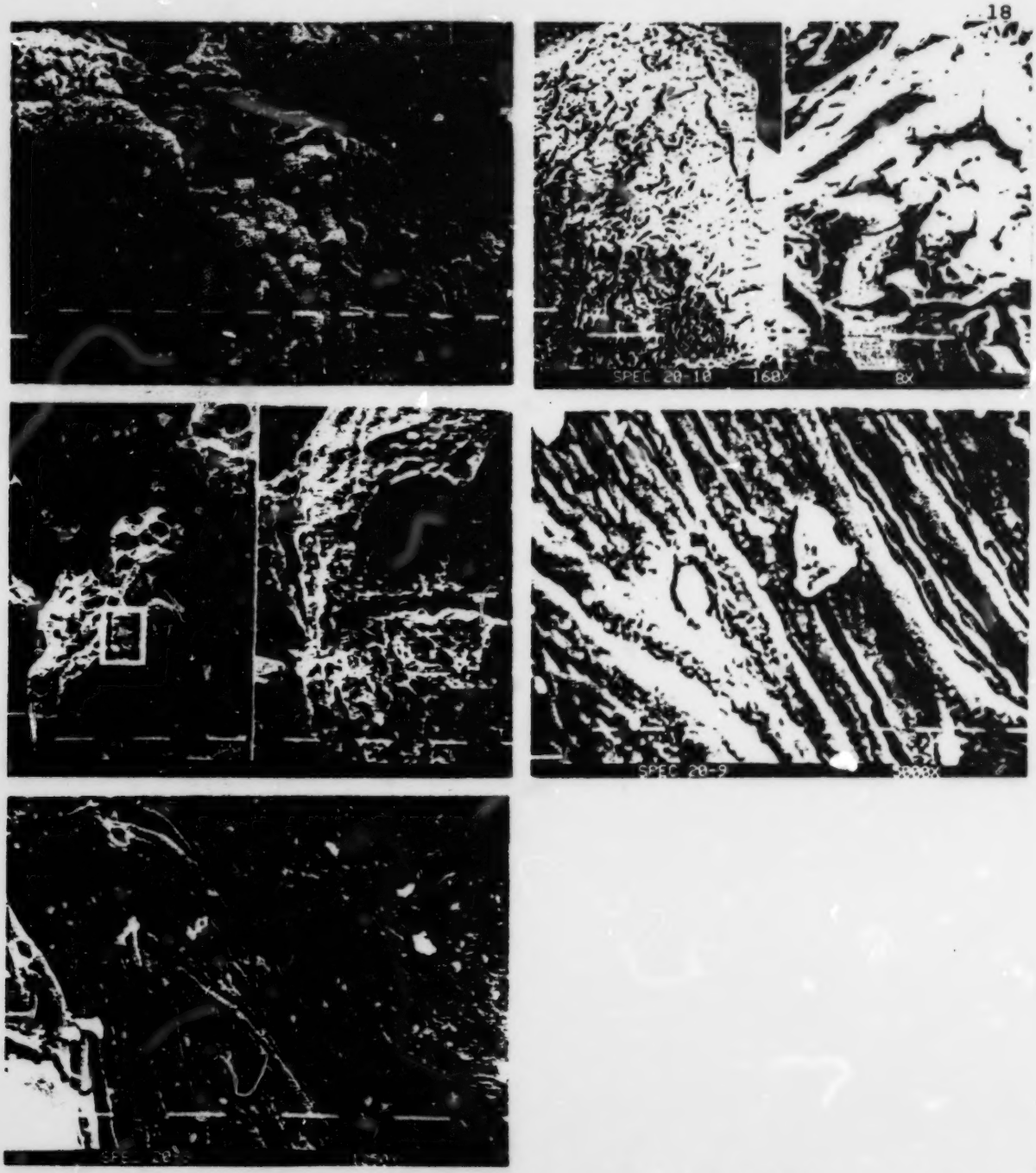


Fig. 14 SEM micrographs of Re-1 coke after potassium impegnation (5.4% wt. K). Specimens were exposed to moisture-saturated air in a dessicator which contained water at room temperature for 500 hours and followed by soaking in water at room temperature for 24 hours.

1	2
3	4
5	

Photograph 3: Overall view of pore and fracture surfaces.

Photographs 1 & 2: Cracks and microporosity.

Photographs 4 & 5: Pitting and cracks on pore surfaces.

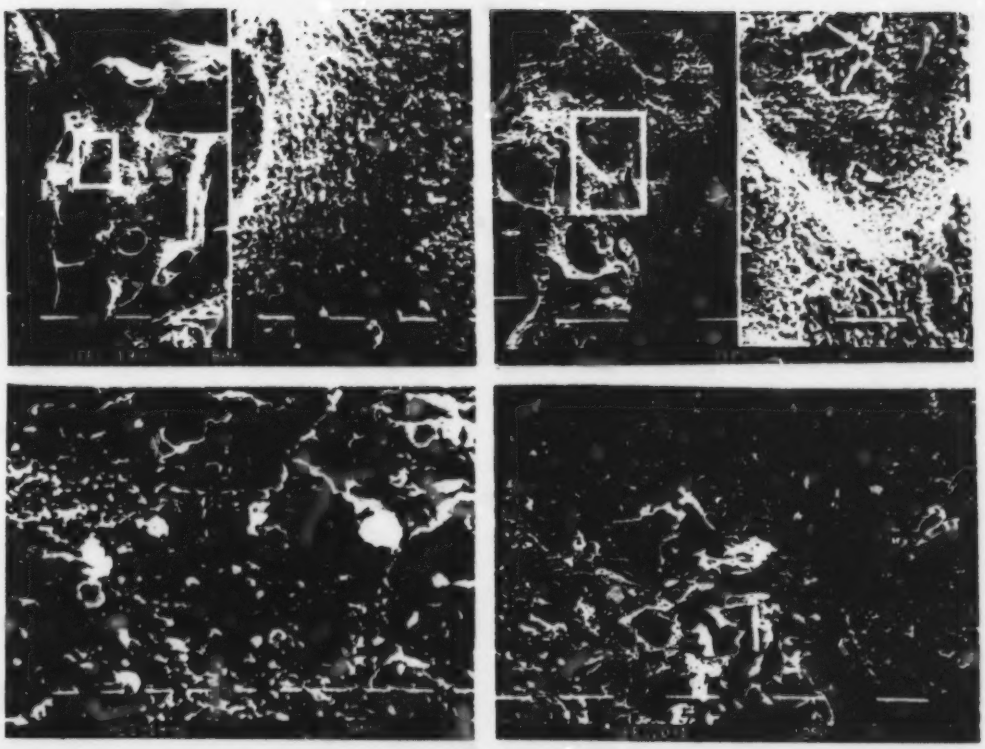


Fig. 15 SEM micrographs of specimens after potassium and moisture absorptions, and washing as described in Fig. 14.

1	2
3	4

Photographs 1 & 3: Al-3 coke (5.7% wt. K) corroded surfaces. Flat new phases above pores.

Photographs 2 & 4: Re-1 coke (5.4% wt. K). Similar appearance.

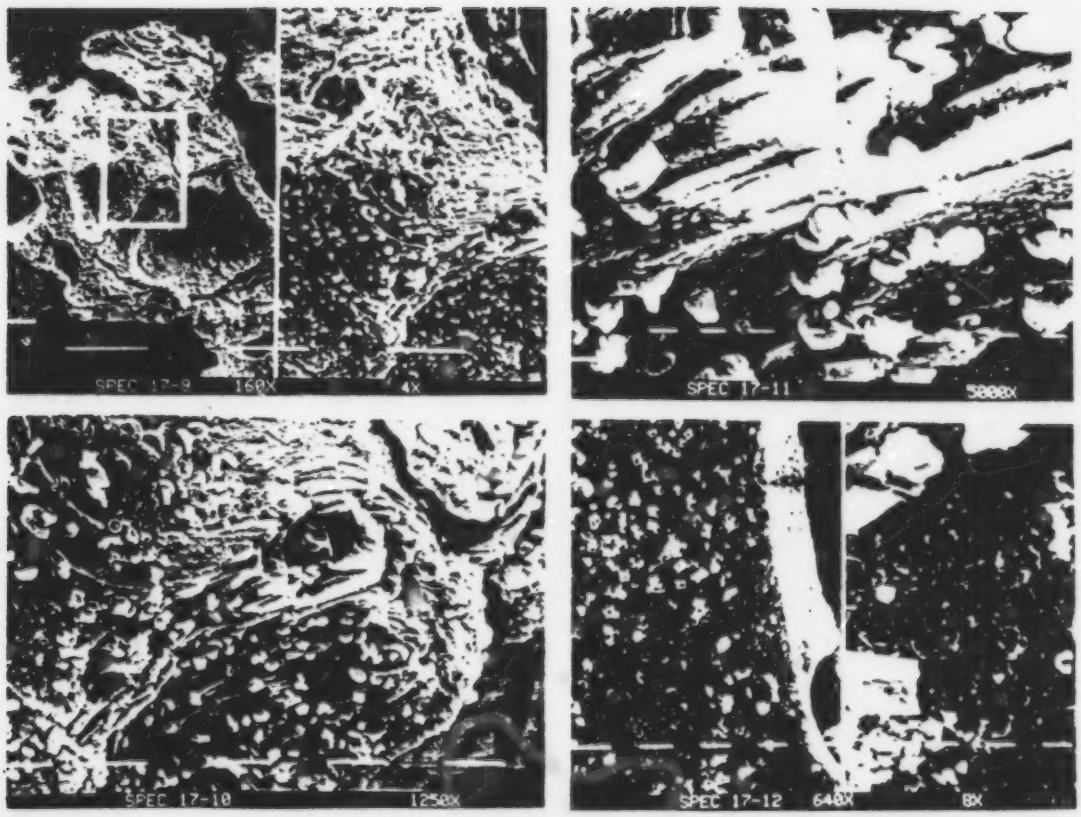


Fig. 16 SEM micrographs of A1-1 coke after potassium absorption (5.2% wt. K) followed by moisture absorptions and washing as described in Fig. 14.

1	2
3	4

Photograph 1: Both types of surfaces covered by particulate new phases.

Photographs 2 & 3: Separation of layers of carbon visible on fracture surface.

Photograph 4: Particulate new phases above very fine pores on a pore surface.

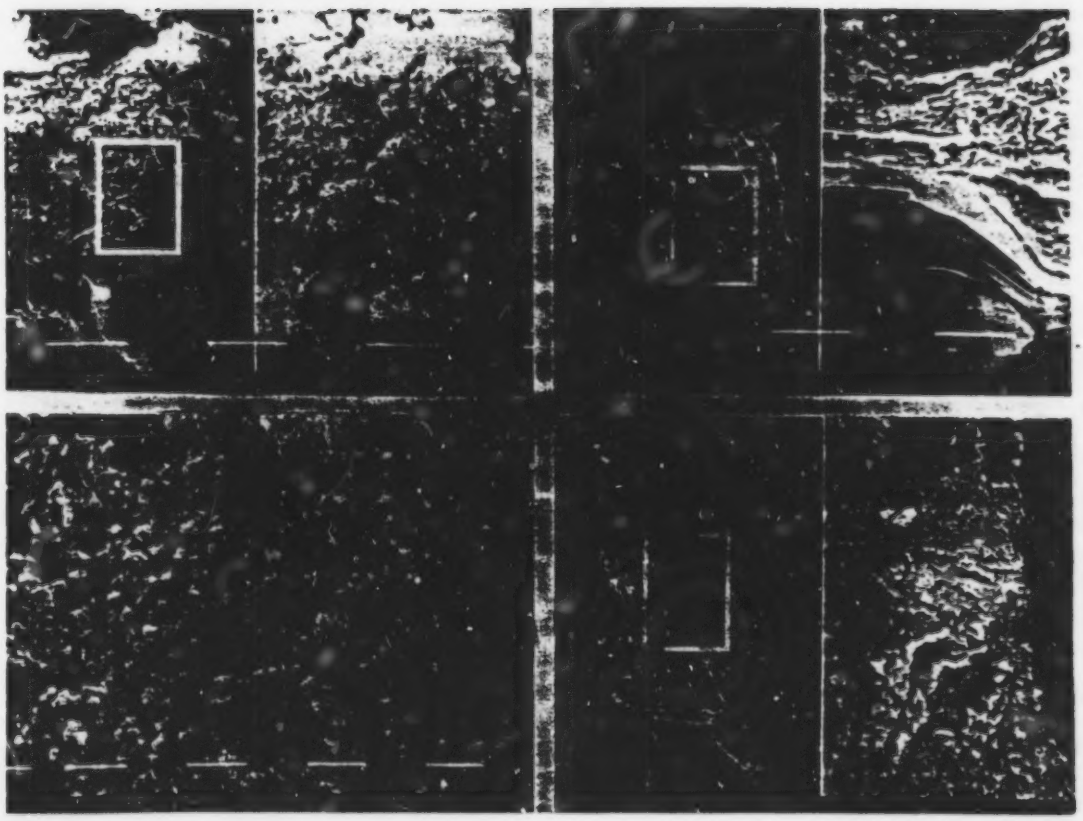


Fig. 17 SEM micrographs of A1-1 coke similarly treated as described in Fig. 16. The new phases appear to be completely removed. Disruptions of the original coke structure, particularly on the fracture surface, are visible.

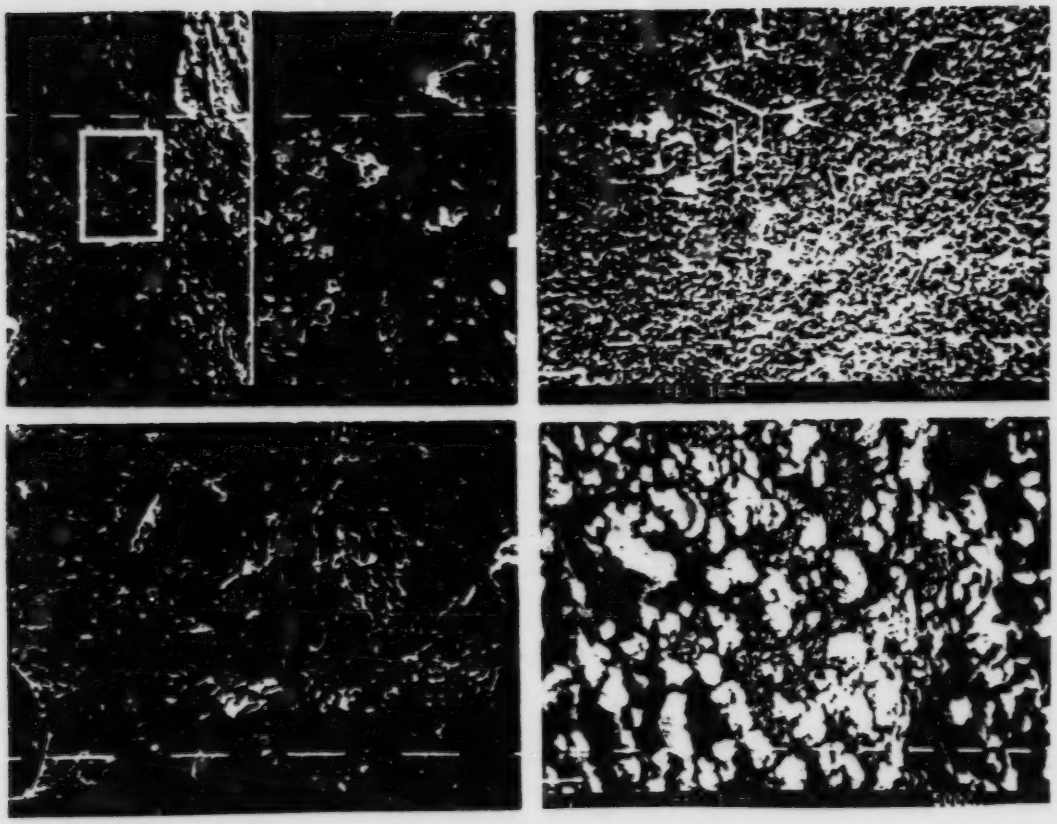


Fig. 18 SEM micrographs of A1-2 coke after potassium (6.1% wt. K) and moisture absorptions and washing as described in Fig. 14.

1	2
3	4

Photographs 1 & 3: Growth of plate-like new phases and fine cracks.

Photographs 2 & 4: Growth of particulate and needle-like new phases and very fine pores.

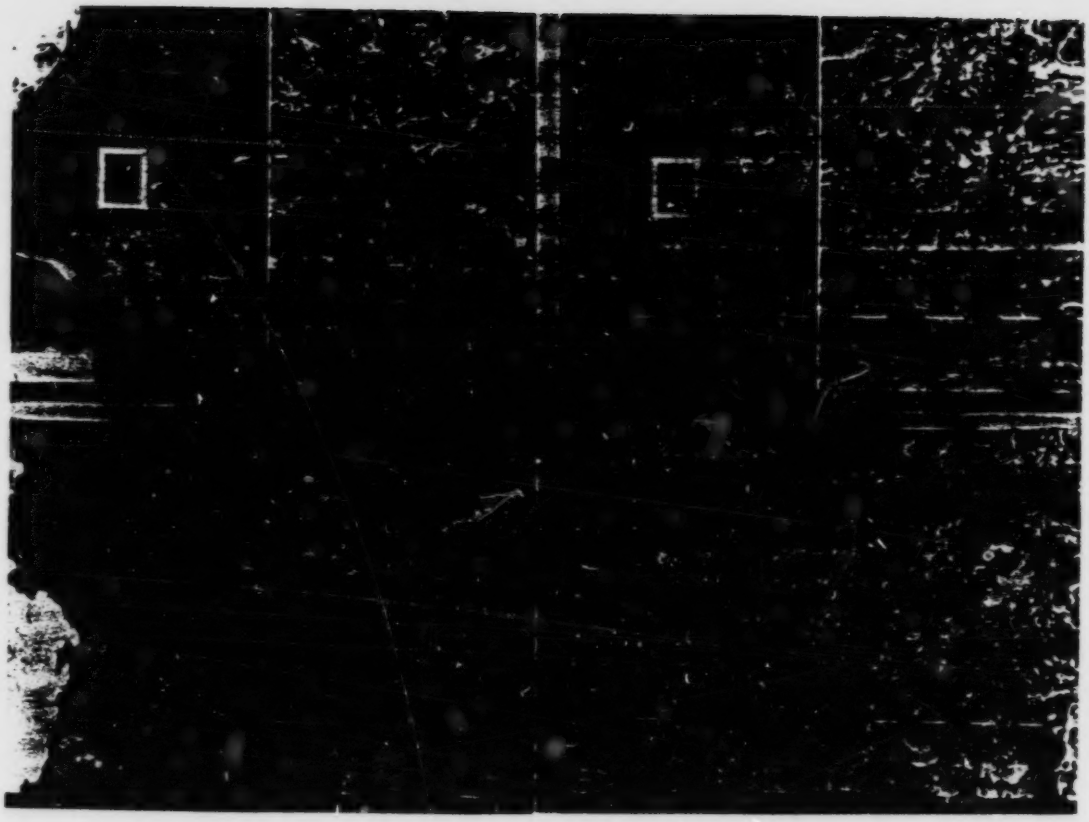


Fig. 19 SEM micrographs of A1-3 coke after potassium (5.7% wt. K) and moisture absorptions and washing as described in Fig. 14.

1	2
3	4

Photographs 1 & 3: Growth of new phases above fine pores on a pore surface.

Photographs 2 & 4: Separation of layers of carbon visible on fracture surfaces.

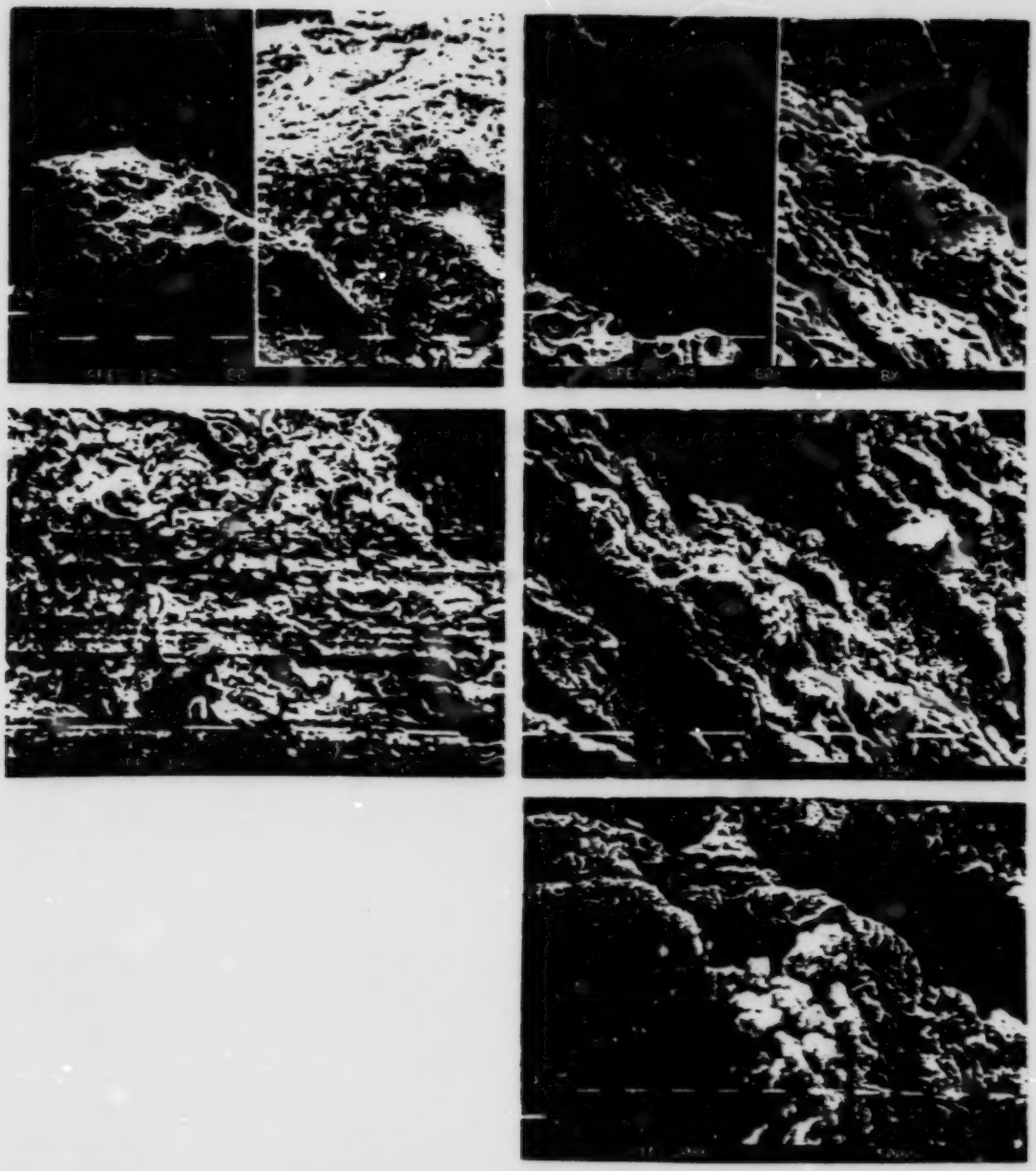


Fig. 20 SEM micrographs of Al-3 coke after potassium (5.7% wt. K) and moisture absorptions and washing as described in Fig. 14. Similar specimens as shown in Fig. 19 except for the absence of new phases. The disruptions on all surfaces in the form of fine cracks and pit-like fine pores are generally visible.

Fig. 21 SEM micrographs of A1-1 coke after potassium (5.2% wt. K) and moisture absorptions and washing as described in Fig. 14. Unusual features showing some very dense crystals separated by gaps and columnar structure.

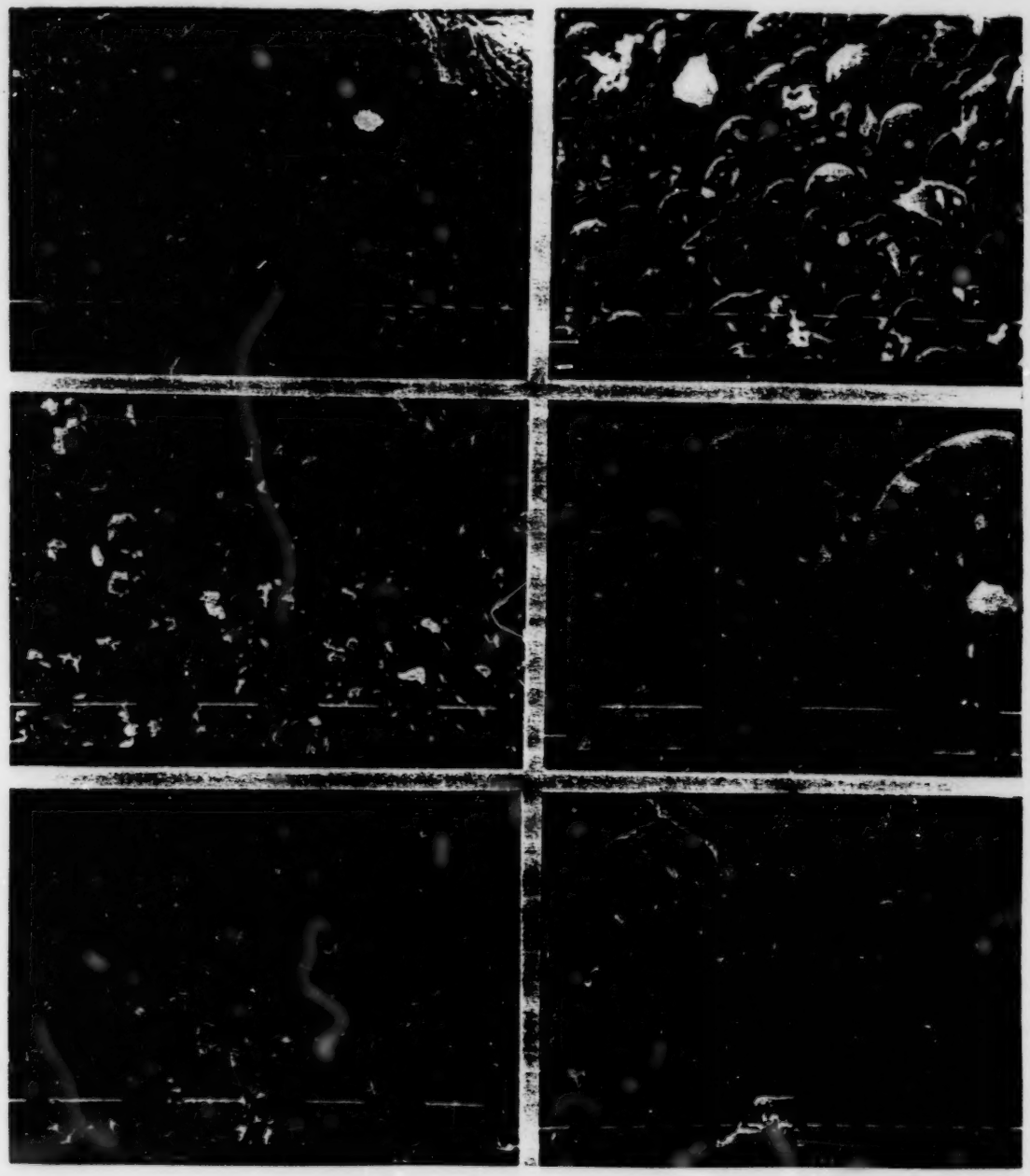


Fig. 22 SEM micrographs of Re-1 coke as-received and Al-3 coke highly oxidized.

1	2
3	4
5	6

Photographs 1 to 5: Mesophase in Re-1 coke.

Photograph 6: Al-3 coke with 47% burn-off. The layer of carbon as the original pore surface was very resistant to oxidation.

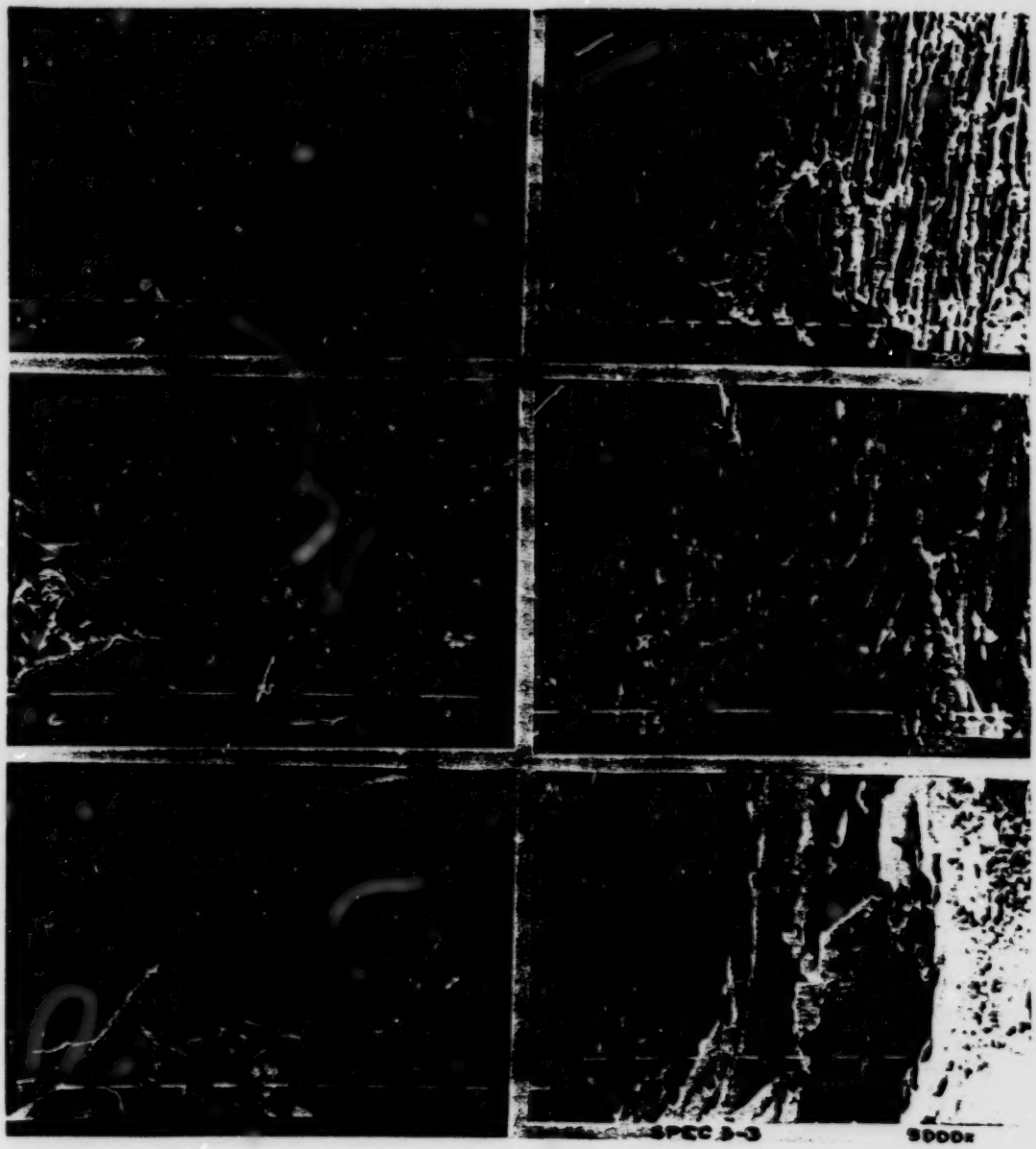


Fig. 2? SEM micrographs of cokes as-received. Features would lead to preferrential attack during oxidation.

1	2
3	4
5	6

Photographs 1, 3 & 5: Re-1 coke shows bundles of very dense carbon crystals separated by long channels for gas diffusion.

Photographs 2, 4 & 6: Al-1 coke shows higher porosity at boundary between domains of different textures.

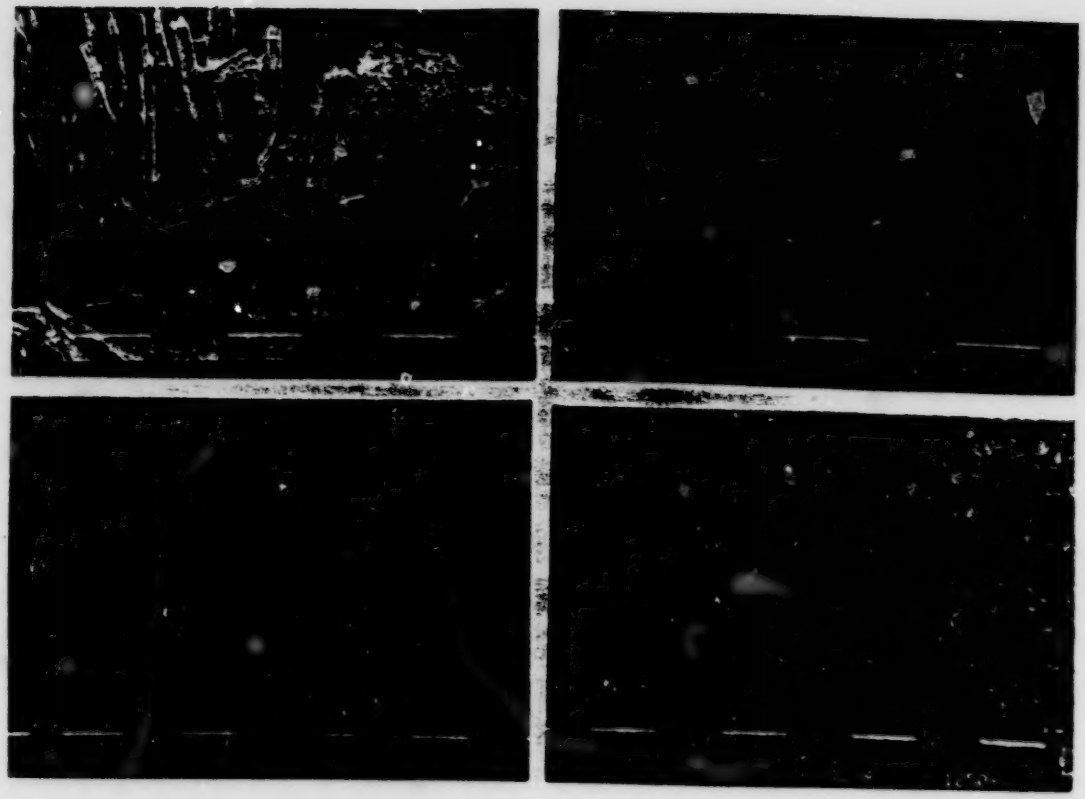


Fig. 24 SEM micrographs of A1-3 coke after potassium impregnation (4.0% wt. K) and oxidation (49% burn-off). Bundles of fibrous materials remained, indicating they were rather resistant to oxidation.

4. SPECIFIC SURFACE AREA MEASUREMENTS

Our work on surface area measurement was carried out by two methods, namely, B.E.T. nitrogen absorption and moisture absorption at room temperature.

A. B.E.T. Method

Preliminary work was carried out with the simple apparatus for oxide powders. The results suggested that these might be a general correlation between the specific surface area of coke specimens and their reactivity with respect to carbon dioxide. Due to the inflexibility of our instrument and inadequacy in its de-gassing cycle, we decided to use the equipment in Dr. P.L. Silveston's laboratory at University of Waterloo.

Many experiments were carried out at the University of Waterloo; up to the present time, no reliable data have been obtained. Dr. Silveston was on sabbatical leave. The service man from the instrument manufacturer was called in a few times. In the past year, the equipment was often not in satisfactory working order and sometimes, due to personnel problems no reliable data could be claimed. Some of the data obtained under these conditions have been reported in an earlier progress report and are not worthy of being discussed again.

We are very grateful to CANMET not only for the laboratory cokes they provided but also for the specific surface area measurements of these cokes done by the B.E.T. method, as shown in Fig. 25.

B. Moisture Absorption

Moisture absorption, following the procedure adopted by Maru and Lu (Ironmaking & Steelmaking, 1980, pp. 257-267) was carried out on all cokes investigated. However, only CANMET cokes were investigated under isothermal conditions with the use of a large water bath with an electrical heating device. As examples, results obtained under isothermal conditions, instead of

at room temperatures, are presented in Figs. 26-31 and summarized in Fig. 25. The results obtained at room temperature on cokes S1 to S8 are given in Fig. 32.

The kinetics of moisture absorption depends on the properties of coke specimens and temperature. At 25°C, moisture absorption by laboratory cokes is slow in comparison with commercial cokes, which reaches saturation at about 500 hours. Kinetics of moisture absorption increased significantly in all cases when the temperature was raised to 30°C. The eventual "saturated value of moisture absorption" is essentially the same for these two temperatures, as shown in Fig. 25.

There is no correlation between B.E.T. surface area and saturated moisture absorption among the ten cokes investigated; see Fig. 25. On the other hand, moisture absorption by specimens after 20% burn-off has an excellent relationship to B.E.T. surface area before oxidation; see Fig. 25. One may suggest that partial gasification of carbon in the coke samples under investigation could widen micropores or channels which were accessible to nitrogen but not to H_2O.

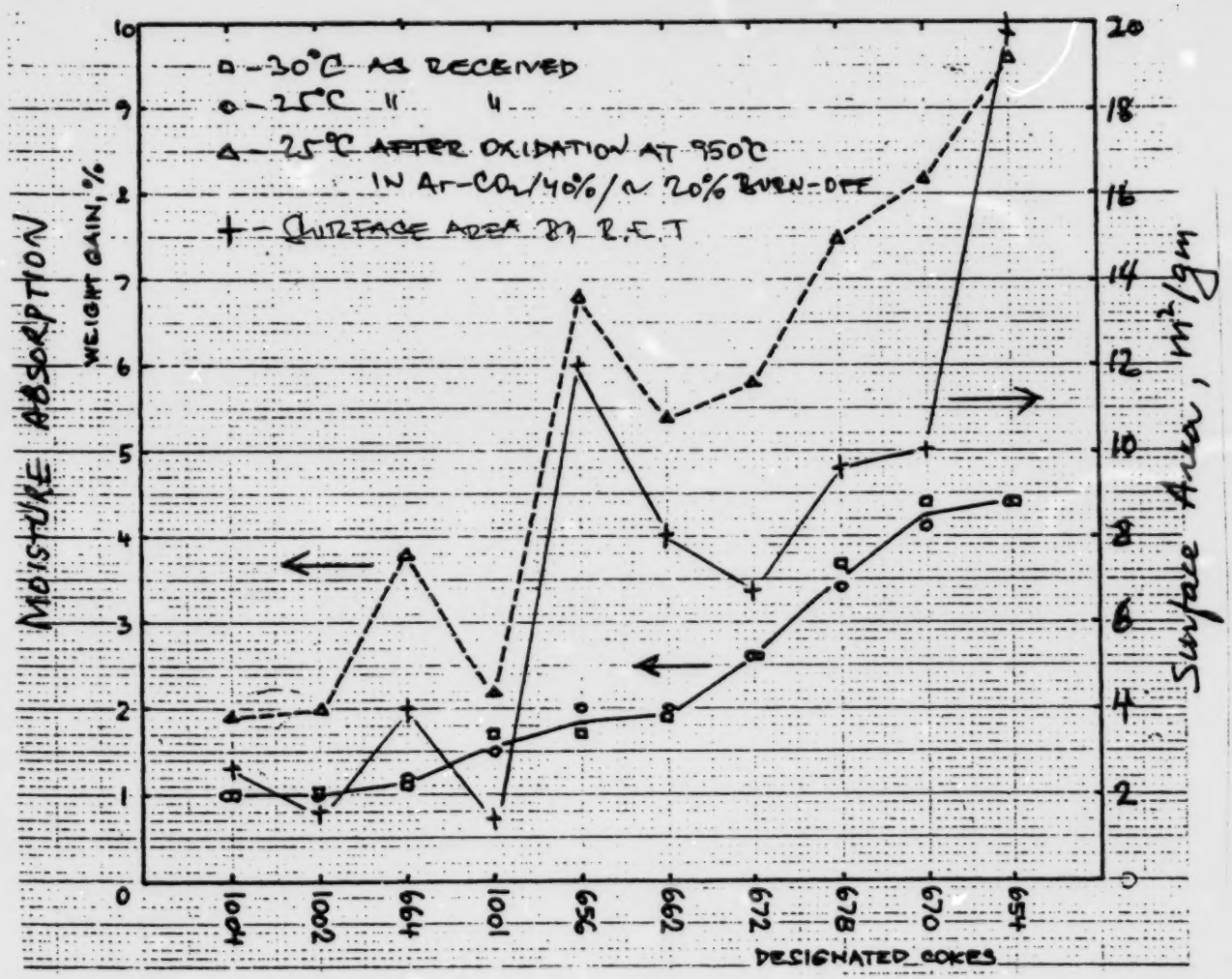


Fig. 25 Comparison of specific surface area measured by B.E.T. method, and moisture absorption by coke specimens.

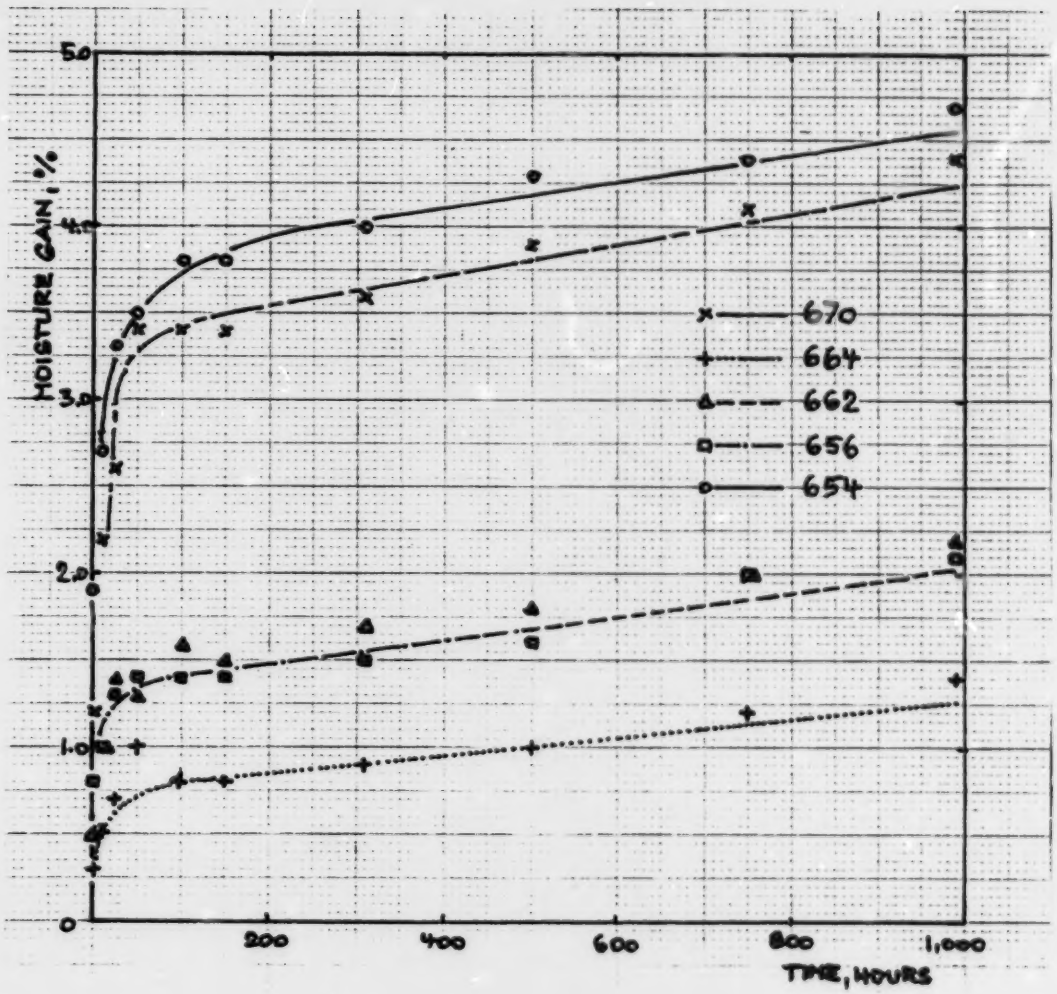


Fig. 26 Moisture absorption of CANMET cokes at 25°C.

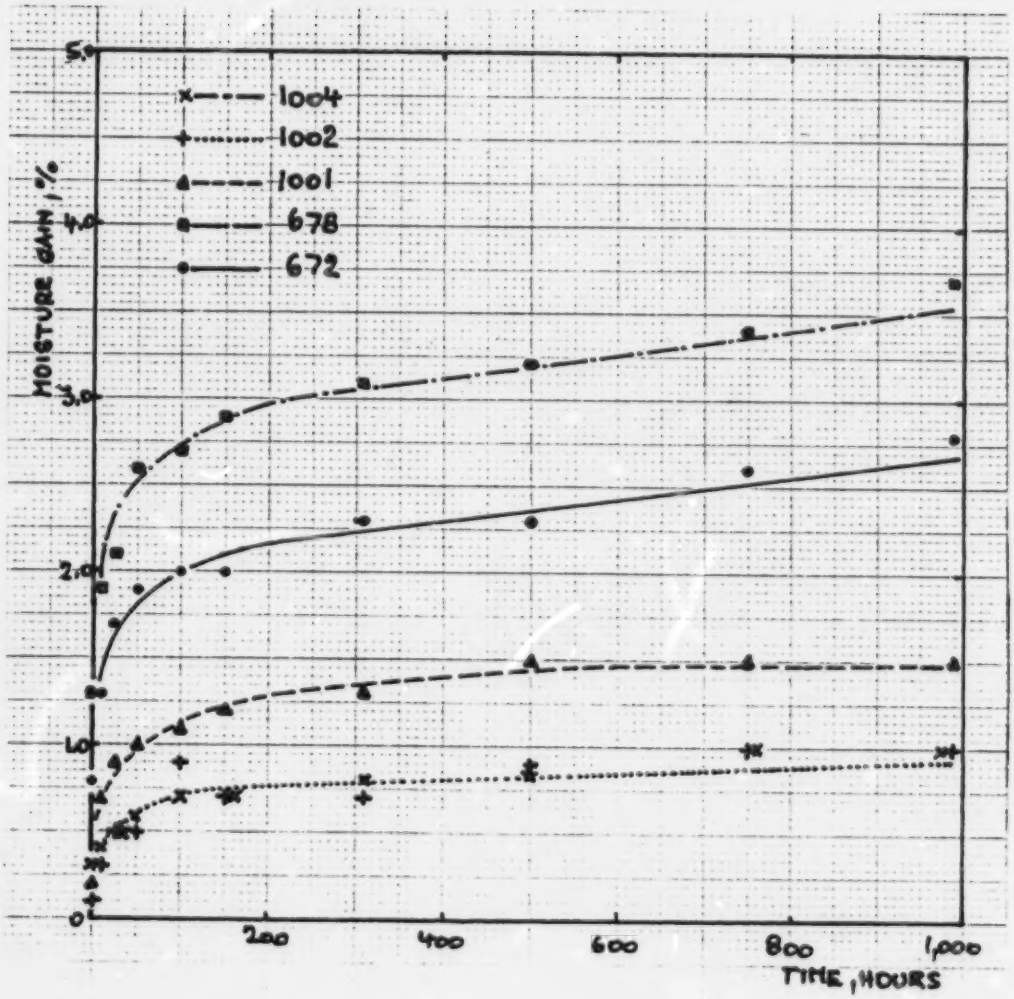


Fig. 27 Moisture absorption of CANMET cokes at 25°C.

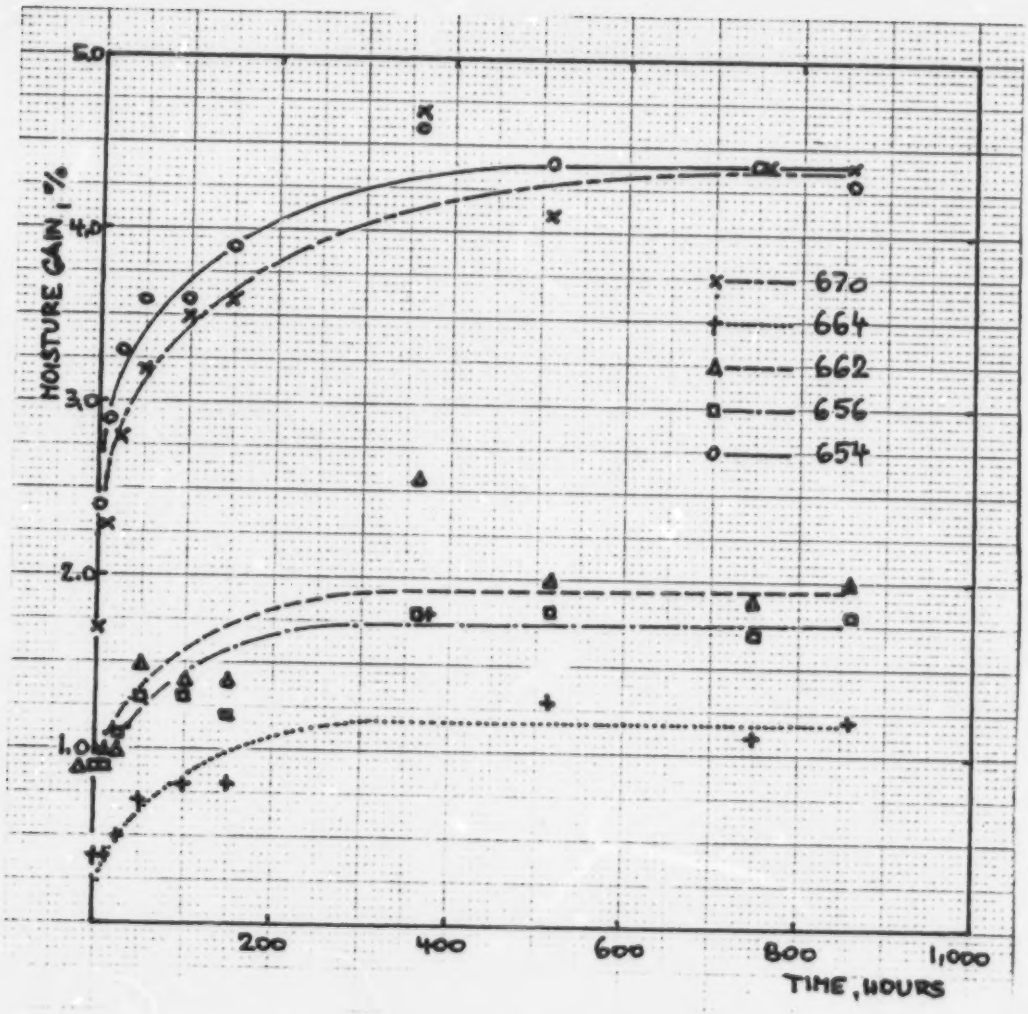


Fig. 28 Moisture absorption of CANMET cokes at 30°C.

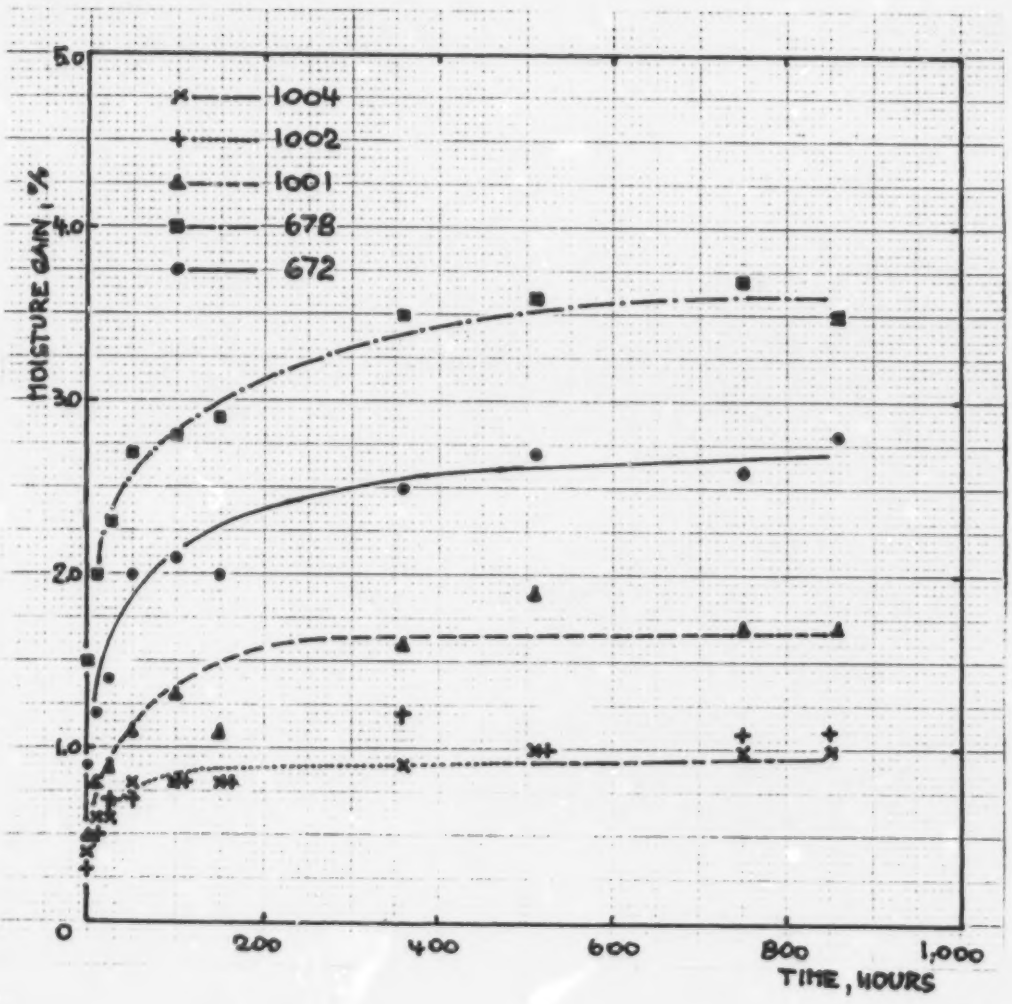


Fig. 29 Moisture absorption of CANMET cokes at 30°C.

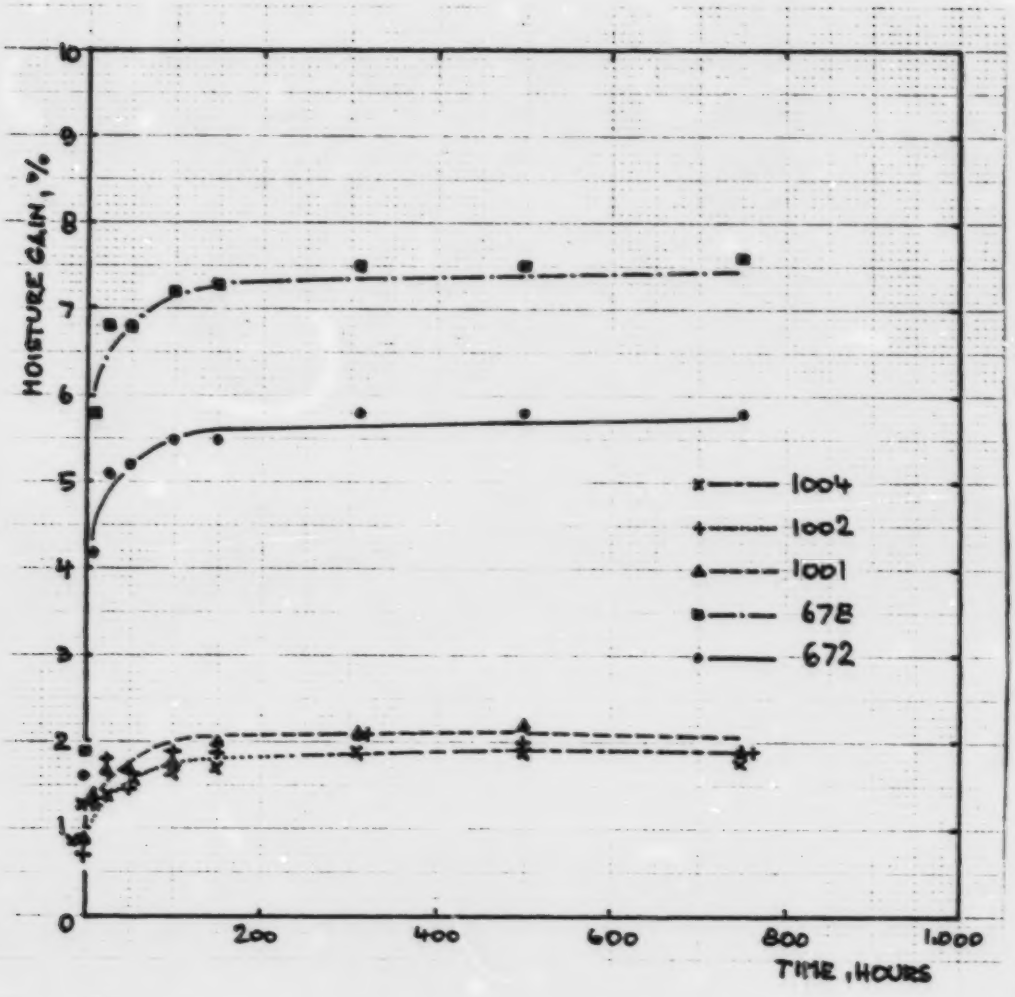


Fig. 30 Moisture absorption of CANMET cokes at 25°C after 20% burn-off at 950°C, Ar-CO_2, 60%-40%.

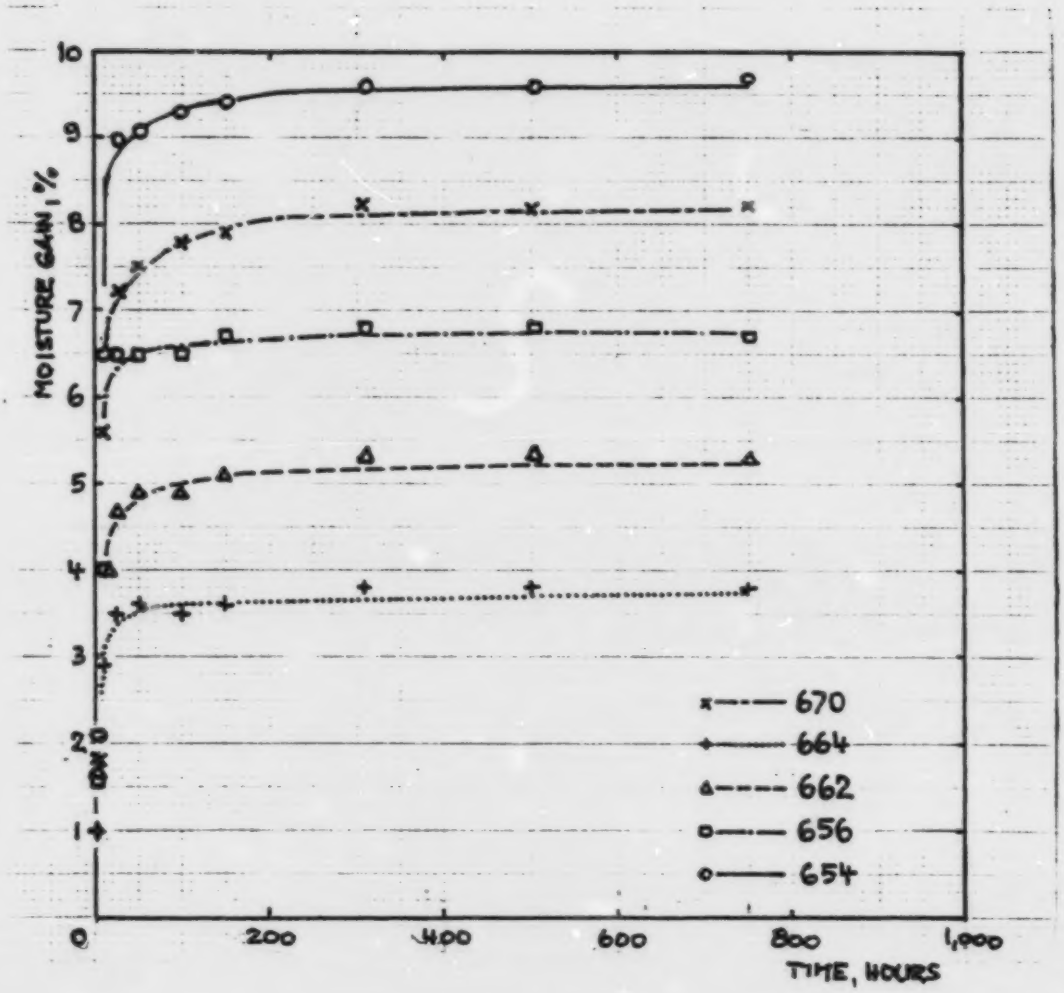


Fig. 31 Moisture absorption of CANMET cokes at 25°C after 20% burn-off at 950°C, Ar-CO_2, 60%-40%.

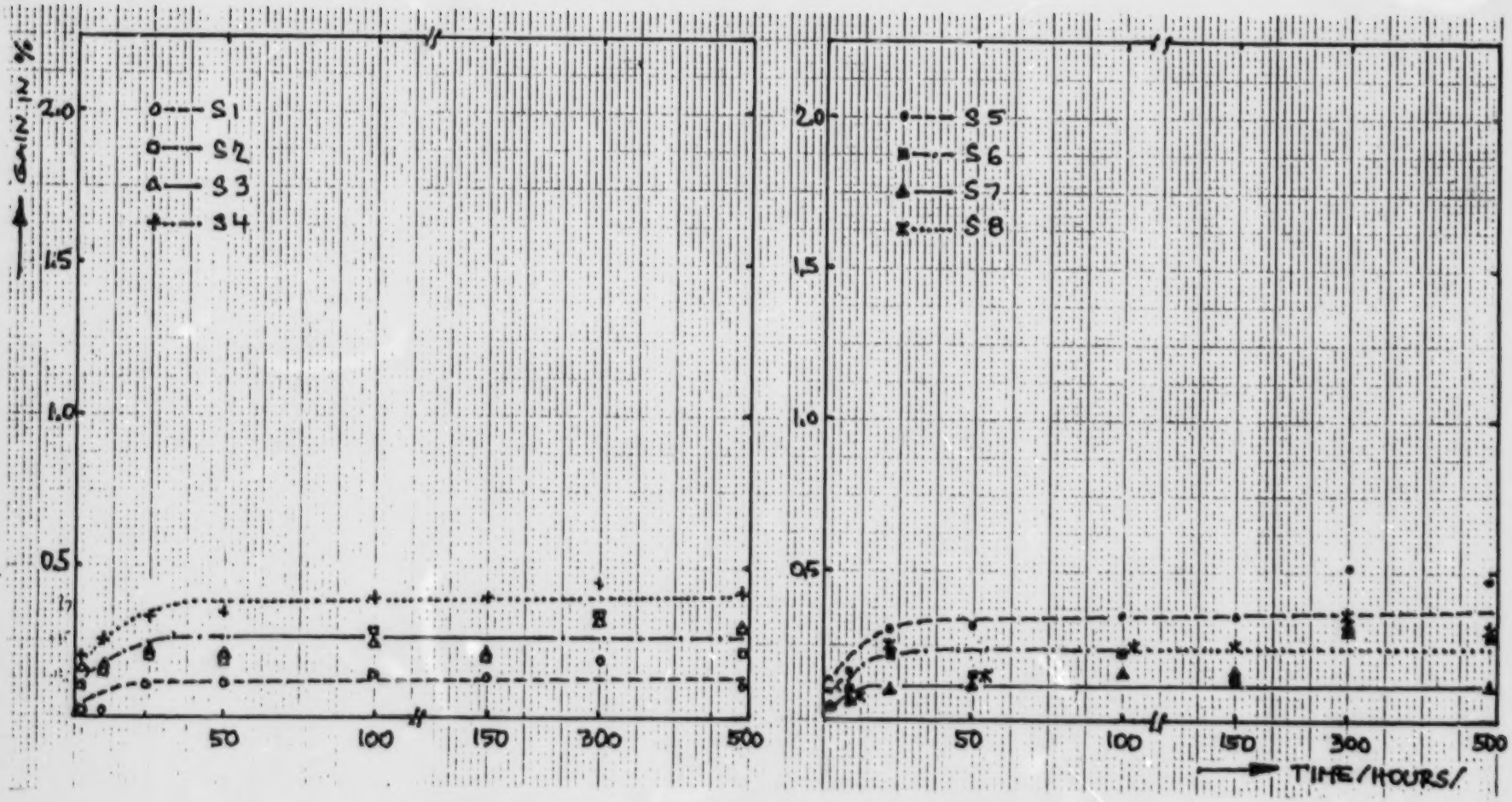


Fig. 32 Moisture absorption of commercial cokes S1 to S8.

5. CHEMICAL REACTIVITY AND SPECIFIC SURFACE AREA

Chemical reactivity was measured in terms of weight loss (% wt.) when coke powders were exposed to an atmosphere of Ar-CO_2 (40%) at 950°C for a given length of time. Two equivalent methods are used to present data, i.e., in Fig. 33 and 34 for CANMET cokes and in Table I for commercial cokes S1 to S8.

Data points in Fig. 33 for each coke form straight lines which indicate that after initial periods, the reaction rates are independent of reaction time (and degree of burn-off) under conditions investigated. For very reactive cokes (e.g., 670, 678) rate of oxidation decreases with the increase of reaction time to an essentially constant value. On the other hand, for cokes 656 and 664 the rate of oxidation increases with time to a stable value. In standardized experiments, for the purpose of comparison, an arbitrary length of reaction time has often been chosen by individual authors. The overall average reaction rates as functions of degree of burn-off or reaction time, are shown in Fig. 34. In Figs. 35 to 38, the reactivity is expressed in degree of burn-off after four hours of reaction.

The data for cokes S1 and S8 as listed in Table 1 are self-explanatory. However, it must be pointed out that as part of a routine procedure, these commercial coke samples were thermally treated before oxidation experiments. Thermal treatment was carried out at 950°C under purified argon atmosphere for 10 minutes.

After analyzing all data obtained up to the present time, it was determined that no general relationship exists between reactivity and specific surface area by B.E.T. method or by moisture absorption. When the laboratory cokes were divided into three groups based on the origin of coals, excellent correlations emerged; see Fig. 35 for B.E.T. surface area and Fig. 36 for

moisture absorption. With respect to cokes 654 and 656 and cokes 1001 to 1004 moisture absorption data correlate with reactivity better than with B.E.T. surface area. One may suggest that not all surfaces measurable by the B.E.T. method are active in CO_2 oxidation under conditions investigated in the present work.

After dividing commercial cokes S1 to S8 into two groups based on batteries from which cokes were made, in the absence of a better basis, correlations between reactivity and moisture absorption were obtained and are shown in Fig. 37. The results obtained on other commercial cokes are given in Fig. 38. Knowing that S-C was originated from a different blend and a new tall oven in comparison with S-A and S-B, the correlations in Fig. 38 are very clear and definite.

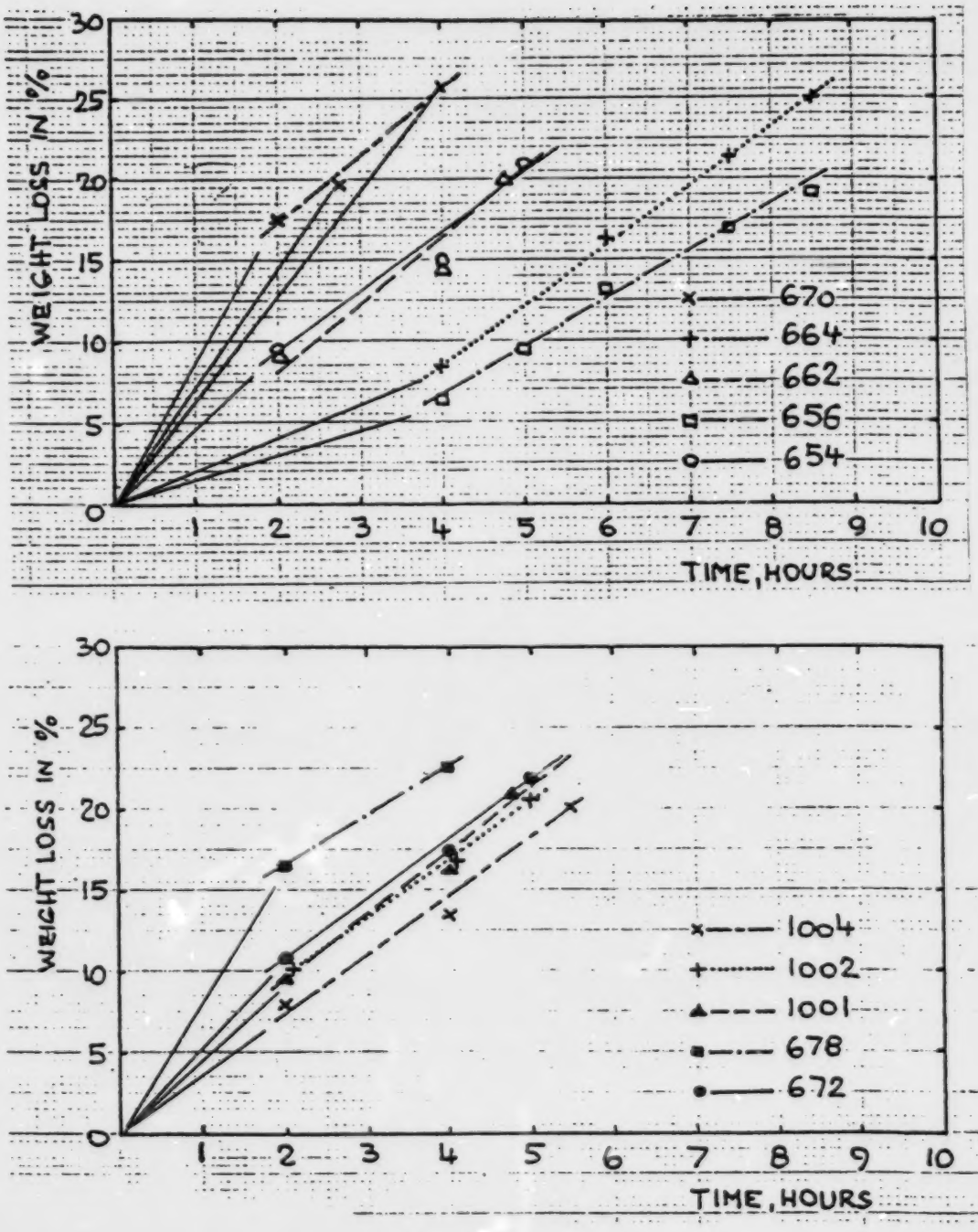


Fig. 33 Oxidation of coke samples in Ar-CO_2 (40%) at 950°C.

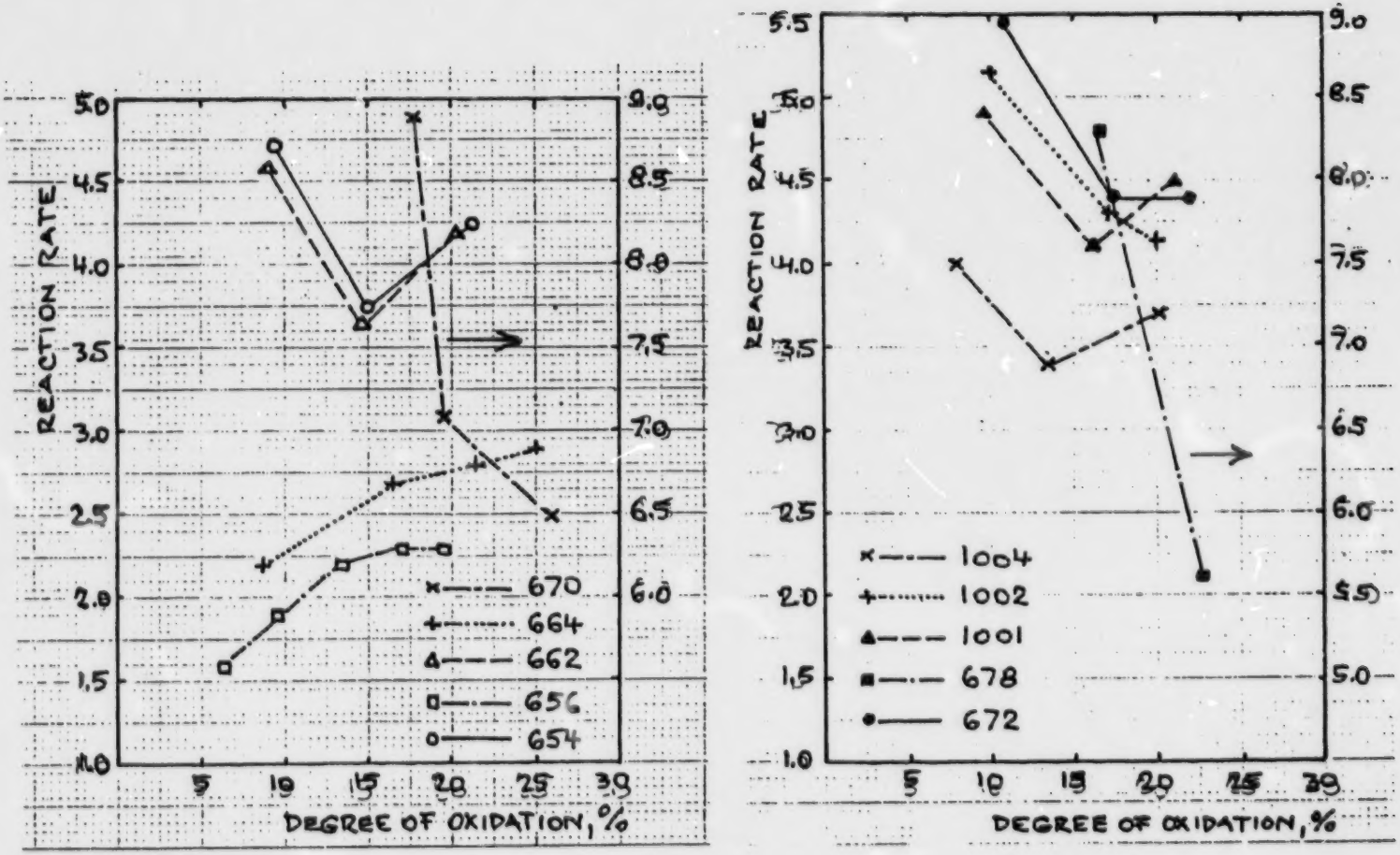


Fig. 34 Average rate of oxidation (% burn-off ÷ oxidation time) vs. degree of burn-off.

Table 1 Oxidation of treated commercial cokes S1 to S8.

CONDITION: HTT 950°C ±2°C; GAS $Ar:CO_2$ => 60%-40% FLOW 4ml/cc.

TIME HOURS	S1 ○			S2 □			S3 △			S4 +			S5 •			S6 ■			S7 ▲			S8 ▼		
	ΔW Gr.	%B.O.	ΔW/TIME	ΔW Gr.	%B.O.	ΔW/TIME	ΔW Gr.	%B.O.	ΔW/TIME	ΔW Gr.	%B.O.	ΔW/TIME	ΔW Gr.	%B.O.	ΔW/TIME	ΔW Gr.	%B.O.	ΔW/TIME	ΔW Gr.	%B.O.	ΔW/TIME	ΔW Gr.	%B.O.	ΔW/TIME
2	.0368	3.7	1.85	.0309	3.1	1.5																		
4													.0882	8.8	2.2	.0514	5.1	1.3	.0733	7.3	1.8	.0756	7.6	1.9
6	.1162	11.6	1.9	.1047	10.5	1.7	.0944	9.4	1.6	.1663	16.6	2.8												
8							.1222	12.2	1.5	.1924	19.2	2.4	.1649	16.5	2.06	.1100	11.0	1.37	.1671	16.7	2.1	.1670	16.7	2.1
9	.171	17.1	1.9	.1542	15.4	1.7							.1849	18.5	2.05				.1992	19.9	2.2	.1967	19.7	2.2
10	.1934	19.3	1.9																					
11				.1834	18.3	1.7																		
12	.264	26.4	2.2	.2313	23.1	1.9	.1992	19.9	1.7	.2996	29.9	2.4												
13																								
13.5																.2525	25.3	1.9						
14																								

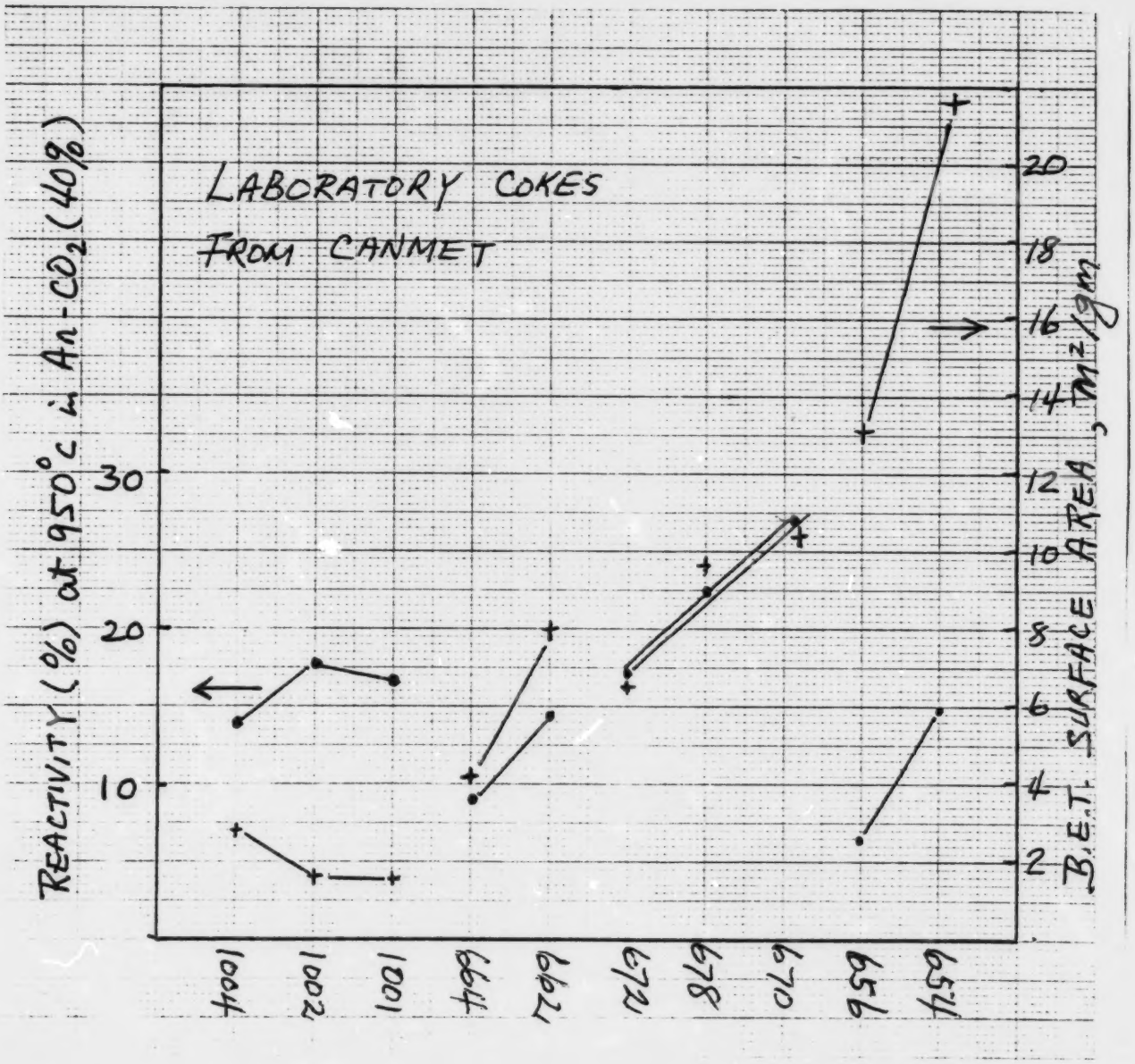


Fig. 35 Reactivity vs. B.E.T. specific surface area.

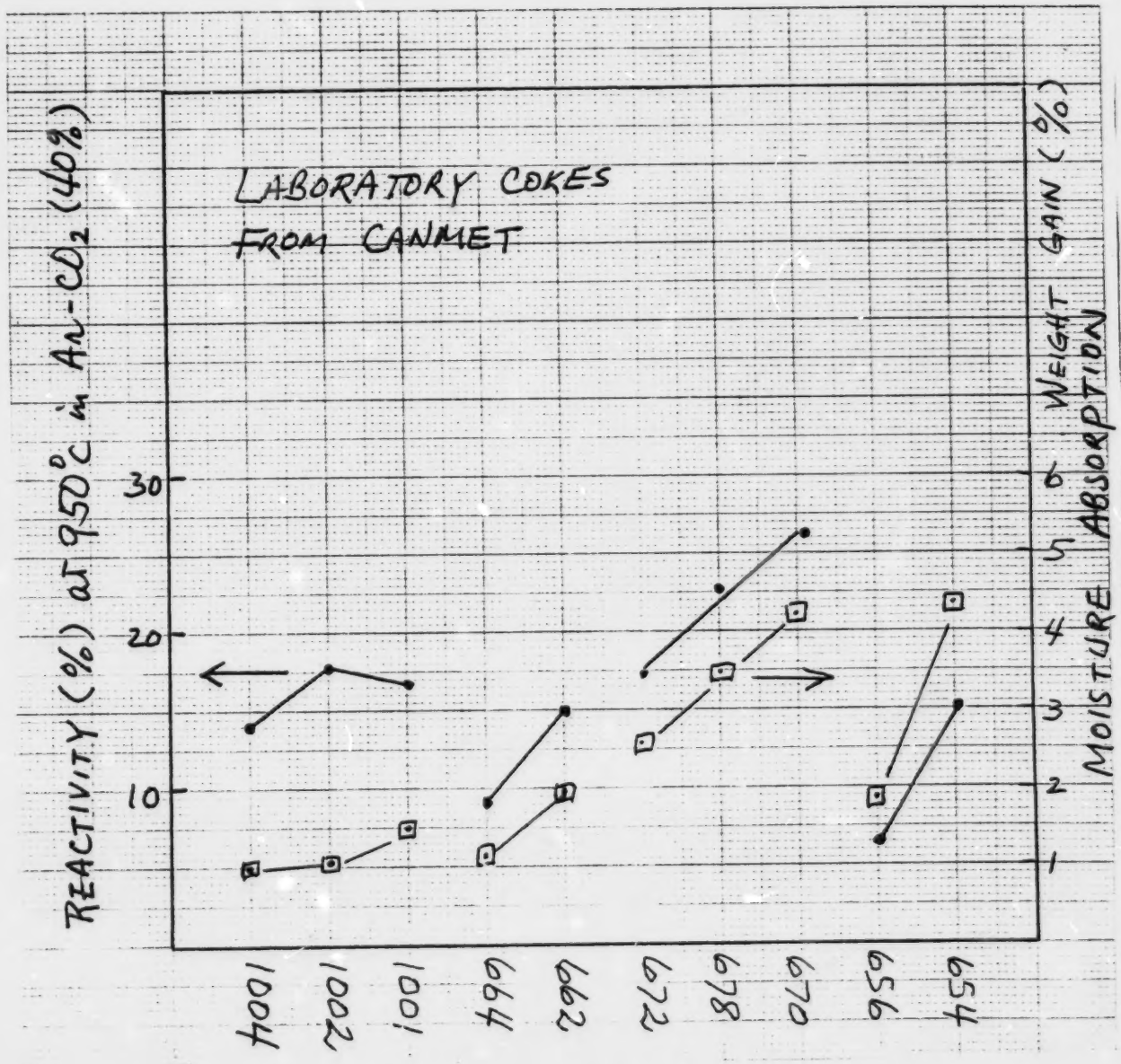


Fig. 36 Reactivity vs. saturated moisture absorption at 25-30°.

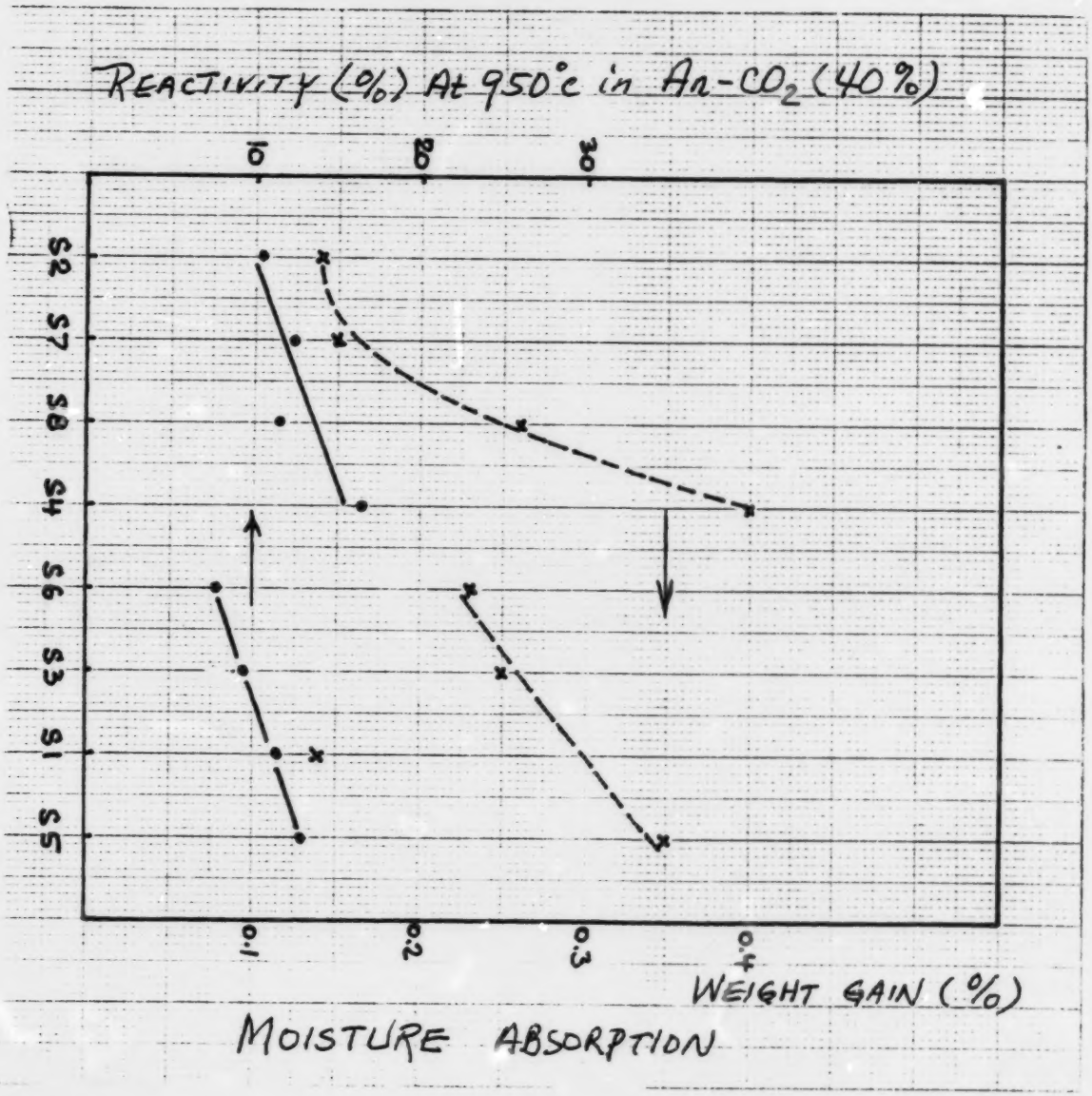


Fig. 37 Reactivity vs. saturated moisture absorption at room temperature.

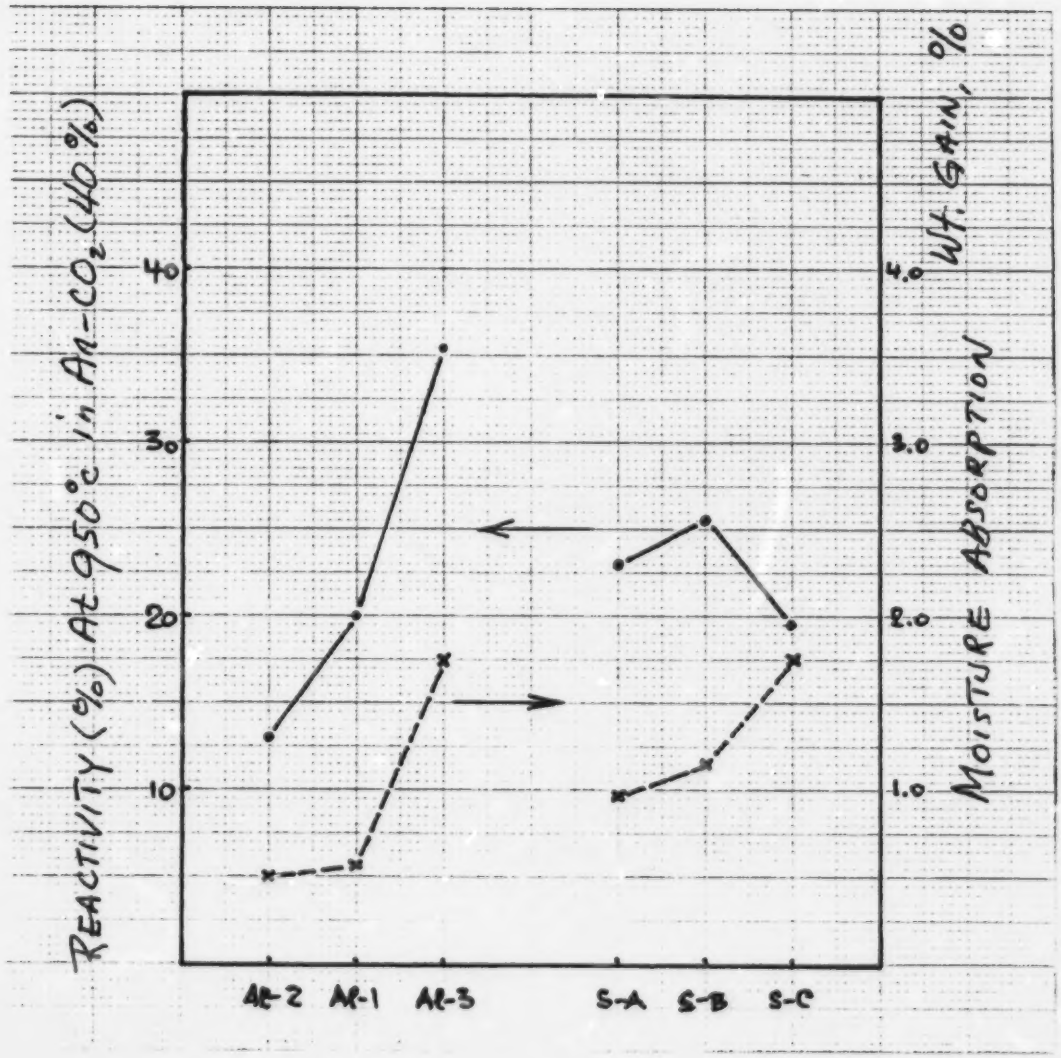


Fig. 38 Reactivity vs. saturated moisture absorption at room temperature.

6. TEXTURE MEASUREMENTS

The texture measurements on CANMET cokes are listed in Table 2. It is generally true that isotropic and inert carbon are more reactive with respect to CO_2. On the other hand, carbons of mosaic structures have lower rates of oxidation and therefore, are enriched in the partially gasified specimens. These results are similar to those reported in the literature.

Table 2 Optical texture analysis of CANMET laboratory cokes.

SAMPLE		190 INERT	SUB TOTAL	MOSAIC F	MOSAIC M	MOSAIC C	SUB TOTAL	GRANULA FLOWTYPE	FLOWTYPE R	FLOWTYPE E	FLOWTYPE F	SUB TOTAL
654	AS RECEIVED	3.3	27.0 30.3	5.0	17.0	39.3	61.3	4.0	–	4.0	0.3	4.3
	OXIDACED	3.0	21.3 24.3	6.7	14.3	49.7	70.7	3.0	–	2.0	–	2.0
656		0.3	27.0 27.3	0.3	5.7	41.0	47.0	19.0	0.3	6.3	–	6.7
		–	23. 23.0	4.3	5.7	52.3	62.3	11.7	..	..	–	3.0
662		–	32.0 32.0	–	–	21.7	21.7	26.0	1.3	13.0	6.0	20.3
		–	23.0 23.0	3.0	7.0	43.3	53.3	11.7	2.0	7.7	2.3	12.0
664		1.7	20.3 22.0	0.3	0.3	13.7	14.3	49.0	2.3	10.3	2.0	14.7
		0.7	22.7 23.3	3.3	2.0	28.0	33.3	32.7	1.3	7.0	2.3	10.7
670		13.0	19.3 32.3	11.7	28.7	24.3	64.7	1.3	0.7	1.0	–	1.7
		2.7	21.3 24.0	8.7	29.7	37.7	76.0	–	–	–	–	–
672		2.3	36.7 39.0	1.7	5.0	53.7	60.3	–	–	0.7	–	0.7
		1.7	24.3 26.0	5.3	9.7	52.7	73.7	–	–	0.3	–	0.3
678		5.3	23.0 28.3	7.7	18.0	40.0	65.7	0.3	0.3	5.3	–	5.7
		3.3	18.7 22.0	11.7	23.0	40.7	75.3	1.7	–	0.7	0.3	1.0
1001		1.0	10.3 11.3	2.7	13.7	42.0	58.3	11.0	4.0	11.3	4.0	19.3
		–	5.3 5.3	1.3	23.7	55.0	80.0	6.0	1.0	5.0	2.7	8.7
1002		4.3	8.7 13.0	11.0	28.3	29.0	68.3	7.3	3.0	7.0	1.3	11.3
		0.7	5.0 5.7	8.0	33.7	43.3	85.0	2.3	2.3	3.7	1.0	7.0
1004		1.7	15.0 16.7	1.7	12.3	36.3	51.3	12.7	3.0	12.7	3.7	19.3
		–	6.7 6.7	0.3	13.3	61.7	75.3	6.7	2.3	7.3	0.7	11.3

7. THE EFFECT OF POTASSIUM

The effect of potassium on the kinetics of oxidation of carbon in cokes has been studied by way of two types of experiments, i.e., potassium impregnation and oxidation by Ar-CO_2 (40%) gas. The "catalytic effect" is so strong that if the reaction temperature were not lowered to 850°C (from 950°C) the rate controlling step would be shifted from chemical reaction control to the case which would be essentially diffusion controlled.

Experiments on all CANMET cokes were carried out but only three low-potassium runs are reported in Table 3. The extremely strong effect of potassium is clearly seen. The other experiments, which all showed strong "catalytic" effect of potassium, have been rejected because of contamination in potassium. The work on the kinetics of potassium absorption is in progress and financially supported by a NSERC Operating Grant.

The results obtained on other commercial cokes are shown in Tables 4 and 5. The extremely strong effect of potassium is certainly confirmed in these experiments.

Table 3 The effect of potassium on coke reactivity.

Oxidizing Gas: $Ar-CO_2$ (40%)

Laboratory Coke from CANMET	662	664	656
Rate of Weight Loss (%/hr) Specimens As Received at 950°C	3.6	2.2	1.6
Amount of K Absorption (%)	0.37	0.15	0.31
Rate of Weight Loss in Oxidation (%/hr) Reaction temperature 850°C	5.7	3.25	5.9

Table 4 The effect of potassium on reactivity of commercial cokes. Al-1, Al-2, and Al-3 are of different peak temperatures in carbonization. Re-1 is a single coal coke.

OXIDATION AT 950°C A_r-CO_2-CO (50-45-5%). TREATMENT WITH 'K' 1000°C-P_K 10^{-2} - 45 min.

TIME HOURS		Al-1	Al-2	Al-3	Re-1	Al-1	Al-2	Al-3	Re-1	
		%BURN-OFF (%)	%BURN-OFF (%)	%BURN-OFF (%)	%BURN-OFF (%)	"K" "K" "K" 1 2 3	"K" "K" "K" 1 2 3	"K" "K" "K"	"K" "K" "K"	
INITIAL WEIGHT 2		1.0000g	1.0000g	1.0000g 18.6%	1.0000g	3.3%-3.4%-3.3% 5.0%-5.2%-6.7%	4.6%-5.1%-5.2% 6.1%-5.3%-7.0%	3.9%-4.0%-4.0% 5.6%-5.7%-6.8%	4.7%-5.4%-6.7% 4.4%-4.9%-5.4%	45'
25		11.0%	6.3%							
3				24.3%						
4				27.4%	19.5%					
6		20.0%	12.8%	35.7%	26.7%					
9		29.2%	20.0%	47.0%	31.0%					
12		37.0%	25.0%	56.9%	36.0%					
OXIDATION		AFTER "K" TREATMENT AT 850°C A_r-CO_2-CO 50%-45%-5%								
30'		2.0 ("K")	2.0. ("K")	2.0. ("K") 15.3% (4.0%)	2.0. ("K")					
45'				26.4% (4.0%)						
1.0		17.2% (3.3%			24.4% (5.4%)					
1.5		29.0% (3.4% 27.1% (3.3%	22.9% (4.6% 23.4% (5.1%	49.3% (3.9%	32.8% (4.7%					

Table 5 The effect of potassium on reactivity of commercial cokes. S-B was made during a strike at low temperature and very long coking time.

OXIDATION AT 950°C Ar-CO_2-CO 50%-45%-5%

SAMPLE		S-A	S-B	S-C					
TIME HOURS		BURN-OFF (%)	BURN-OFF (%)	BURN-OFF (%)					
INITIAL WEIGHT		1.0000g	1.0000g	1.0000g					
2		7.75%	10.3%	8.0%					
4		17.0%	18.0%	14.0%					
6		23.0%	25.7%	19.8%					
8		34.0%	51.5%	30.4%					
		TREATMENT WITH "K" 1000°C - Pk 10^{-2} - 45 min.							
45	WT. GAIN %	3.5% 3.8% 4.7% 1 2 3	4.5%-4.5%-6.1% 1 2 3	4.3%-4.5%-5.7% 1 2 3					
		OXIDATION AT 850°C AFTER TREATMENT WITH "K"							
		B.O. ("K")	B.O. ("K")	B.O. ("K")					
1		13.6% (3.8%)	20.3% (4.5%) 20.3% (4.5%)	13.7% (4.5%)					
1.5		15.4% (3.5%) 19.2% (3.8%)		12.9% (4.3%)					

8. THE EFFECT OF HYDROGEN

In Fig. 39, the effect of particle size of coke powders is shown. In all experiments, size fractions of 0.5 to 0.6 mm were selected. The reactivity of under-sized (0.5 to 0.25 mm) particles has been found to be slightly higher but, due to the many factors involved, may or may not be significant.

Some specimens, after the moisture absorption experiments, were placed in a dryer at 110°C overnight. In every case, the new dry weights were noticeably higher than the dry weights before moisture absorption experiments. This indicated that a small part of water vapour was chemically absorbed. It is conceivable that when the temperature is raised the chemisorbed H_2O will lead to gasification of carbon. The absolute amount of weight loss by this mechanism should not be significant; however, its kinetic effect could be pronounced. This effect due to chemisorbed moisture is clearly shown in Fig. 39. The degradation of commercial coke in the stockpile is well known. It could be one of the contributing factors. This series of experiments naturally led us to examine the effect of hydrogen in the blast furnace on the reactivity of coke.

When hydrogen was introduced into the usual oxidizing gas Ar-CO_2 (40%) which was maintained at constant flow rate, a decrease in the thermodynamic oxidation power resulted. In terms of the changes in composition due to water gas shift reaction, the formation of carbon monoxide and water vapour will lower the concentration of carbon dioxide. It is well known that the presence of carbon monoxide would have a retardation effect on the oxidation of carbon by carbon dioxide.

The induction of hydrogen may have the following consequences:

A. Retardation of gasification: due to a decrease of CO_2 and an increase in CO concentrations.

B. Acceleration of gasification: due to a faster reaction rate with H_2O in comparison with CO_2.

The results with CANMET and commercial cokes are given in Figs. 40 and 41. In general, hydrogen has a stronger effect on laboratory cokes than on commercial coke, particularly cokes 654 and 656. The retardation of gasification due to the presence of CO appears to be weaker than the positive effect of water vapour on these two cokes, as shown in Fig. 40.

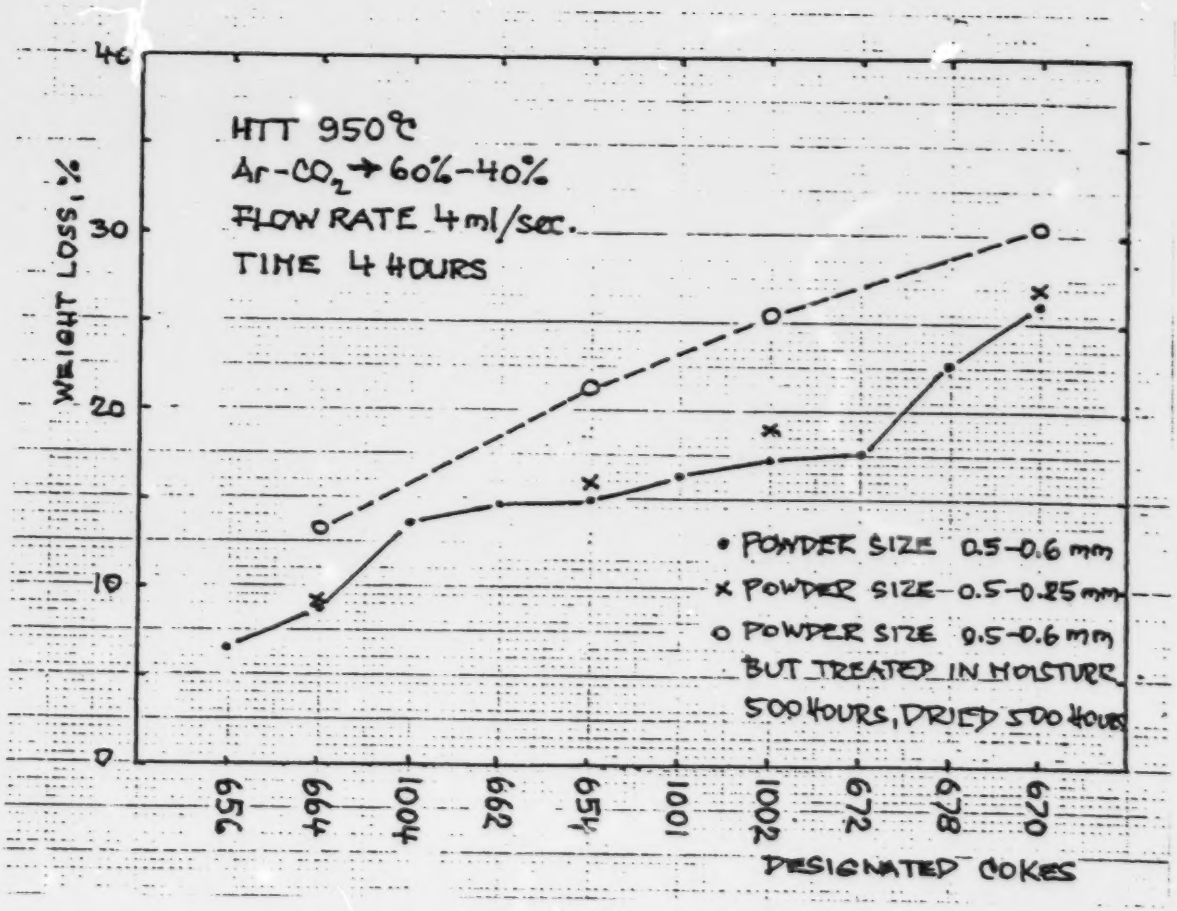


Fig. 39 The effect of particle size and moisture absorption in the kinetics of carbon oxidation.

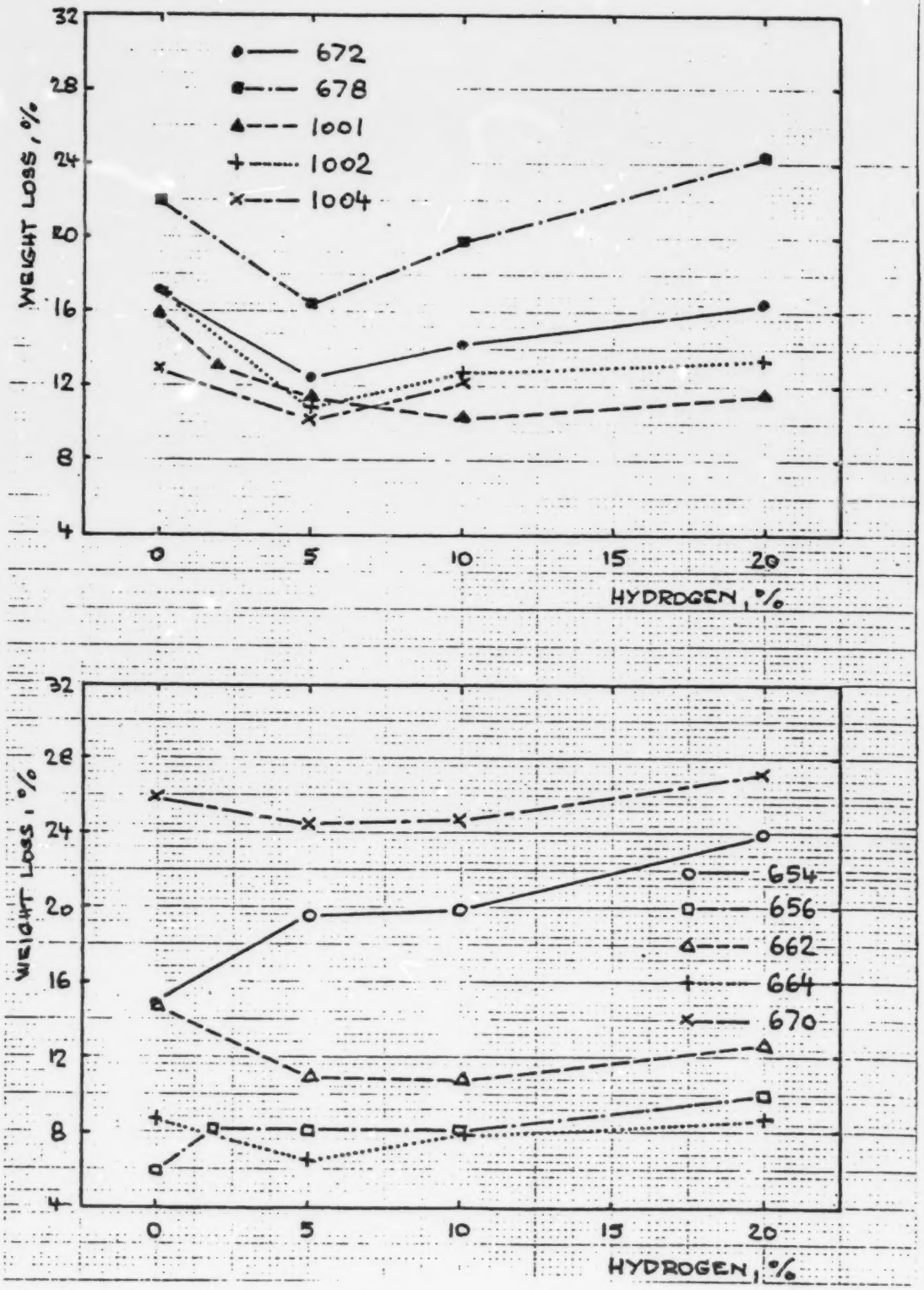


Fig. 40 The effect of the addition of hydrogen to Ar-CO_2 (40%) gas on the oxidation kinetics of CANMET cokes.

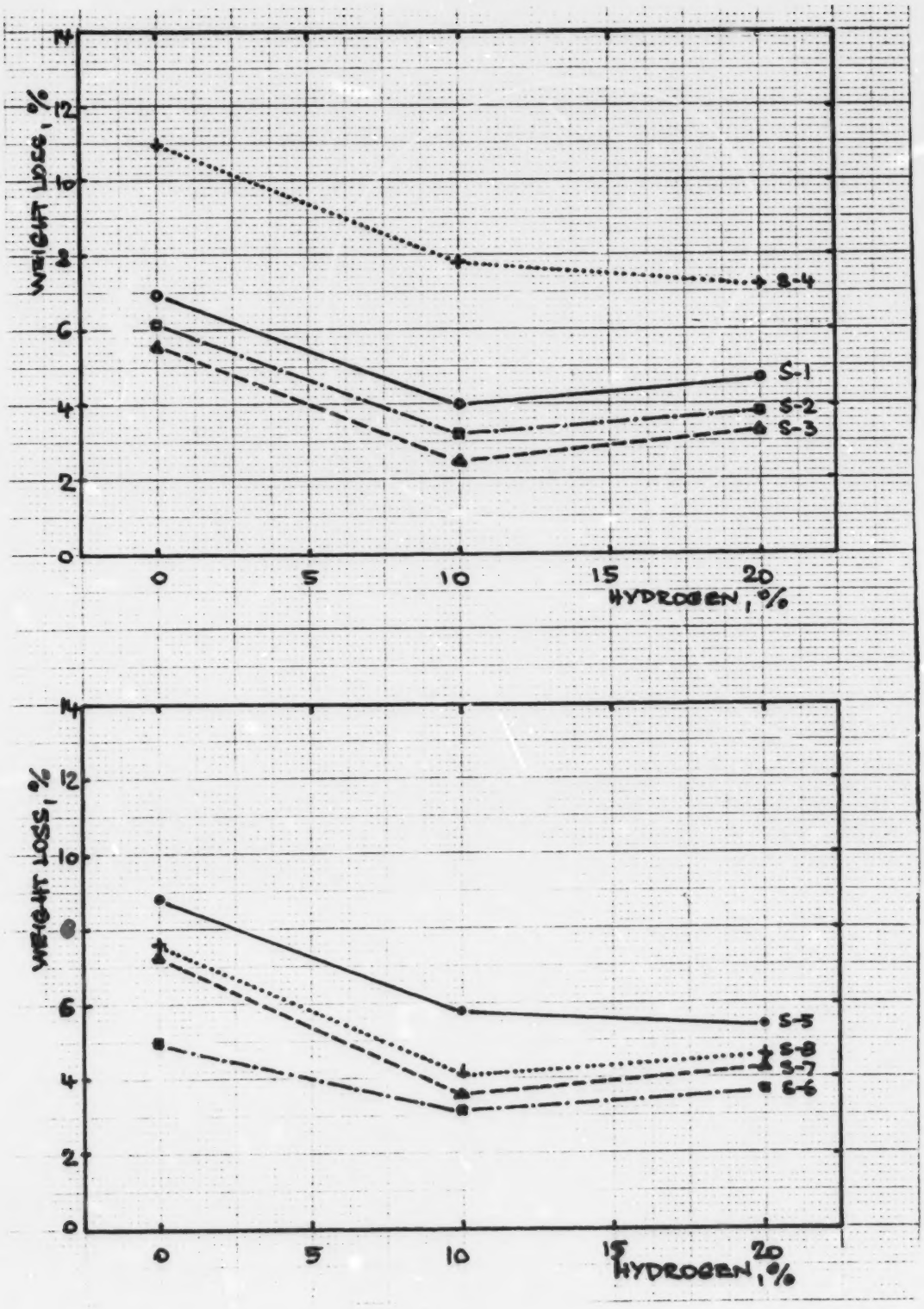


Fig. 41 The effect of the addition of hydrogen to Ar-CO_2 (40%) gas on the oxidation of commercial cokes.

9. ELECTRICAL CONDUCTIVITY MEASUREMENTS

A. Introduction

The causes of degradation of coke in the blast furnace which can be attributed to chemical attack, are gasification by carbon dioxide and the weakening of coke due to the absorption of alkali vapours. With respect to CO_2 oxidation, there are two types of surface in cokes, i.e., fracture surface of the pore wall and pore surface. The potassium enters into the coke and reacts with carbon to form intercalation compounds. The formation of these compounds results in expansion of the carbon structure and leads to the initiation and propagation of microcracks in the coke.

Knowledge of electrical properties of the compounds gives valuable information about the electronic state of the species intercalated in carbon. Ubbelohde and his co-workers[1] measured the electrical conductivity of potassium graphite of various compositions. In much of this work it was found that the uptake of potassium thus brings about a considerable increase in the conductivity. Ottmer et al.[2] measured the electrical conductivity of pressed samples of potassium graphite compounds and graphite as a function of temperature from 100 to 350°K. The conductivities were 10 to 100 times as large as those for pure graphite over the temperature range examined. The conductivities of the potassium-graphite compounds decreased with an increase in temperature.

Our work continues on the differentiation of potassium in coke into two categories, namely, in intercalation compounds and in ash by chemical analytical means. The measurement of the effects of potassium on the conductivity of coke powders offers two opportunities: the positive effect of intercalation compound formation and the negative effect of microcrack formation.

We have developed the equipment to measure the electrical conductivity of coke powders. The equipment and method will be described in this section. Some preliminary results of coke as received and some after potassium adsorption achieved with the use of a new generator, are presented.

B. Coke Samples

In order to study the effect of mechanical pressure on the powder packing and resistance measurements, S-A coke samples of the following four ranges of particle size, have been used:

(i) 150 - 180 μm
(ii) 300 - 355 μm
(iii) 500 - 600 μm
(iv) 850 - 1000 μm

All samples were dried at 100°C for two hours before conducting the electrical conductivity measurements.

C. Apparatus

The apparatus is shown in Fig. 42. The top pressure gauge was sufficiently adjustable to give the required uniform rate of increase of pressure on the electrode. The two electrodes were made of copper. The bottom electrode is a close sliding fit in the glass tubing and is held firmly in position, and the top electrode is a loose sliding fit. The connection is made for the measurement of current and the voltage drop through the four copper wires. The coke powders of measured amounts are contained in the electrode chamber to give packing of various heights which was measured to ± 0.01 mm with a travelling microscope.

D. Method of Measurement

During the measurements, the regulated DC power supply has been used to fit the current at 1 ampere. The resistance R of coke powders can be found from Ohm's Law R = V/I; then, with a knowledge of the cross sectional area of

the electrode chamber (S = 4.82 cm^2) and the slope of the plot of resistance against heights of the column, we could calculate the electrical conductivity (σ) (or the resistivity (ρ)).

E. Pressure Gauge Calibration

The pressure gauge is calibrated with a Univeral Flat Load Cell. It is done by relating the readings of the pressure gauge and the micro cell (mv), (Table 6), and the relation between the load (kg) and the output of the micro cell (mv) (Table 7). From Tables 6 and 7, we could find the calibration line of the pressure gauge and the weight as shown in Fig. 43. Based on this calibration line, the mechanical pressure on the powder packing can be calculated. The extrapolated line does not pass through the origin, owing to friction of the cylinder of the pressure gauge.

F. Experimental Results of Electrical Conductivity

(i) The Effect of Mechanical Pressure on the Coke Resistance

Coke samples in powder form were placed in the electrode chamber. In each run, the total weight of the coke sample was kept constant and the resistance (R) was measured at pressures between 0.74 to 18 (kg/cm^2) for 12 values of pressure.

Figs. 44 to 47 show the effect of pressure on the resistance (R) and the volume change (%) with different particle size. When the pressure was increased up to 15 (kg/cm^2), the volume change continued; however, the resistance approached a constant value. This shows that there is not a particular pressure in the range investigated, above which conductivity of powders would be independent of packing conditions. For practical reasons, all the measurements reported here were carried out under a mechanical pressure of 17 kg/cm^2.

(ii) Electrical Conductivity of Coke Samples as Received

Fig. 48 shows the value of electrical conductivity in three kinds of commercial cokes as received. The measured values of S-A, S-B (made during a strike) and S-C are 11.33, 14.14 and 10.32 ($\Omega^{-1}cm^{-1}$), respectively. The S-B value is highest, because of the residence time of coke in the oven for nearly two days, but the carbonization temperature was substantially lower. This may suggest that the degree of crystallization in coke is more advanced. There are different values between S-A and S-C; this may be attributed to the differences in the type of coal blends in two plants.

The electrical conductivity results are given in Fig. 49 for three commercial coke samples as received with different values of volatile matter (%).

The measured values of A1-1 and A1-2 are slightly different in the range of volatile matter from 0.90 to 1.31 (%). However, electrical conductivity and the remaining volatile matter (%) in coke, and an indirect relation to the final carbonization temperature in this particular case.

(iii) Electrical Conductivity of Coke Samples After Potassium Adsorption

The results of the electrical conductivity (σ) after potassium adsorption are listed in Table 8 and are plotted in Fig. 50. Here, the solid line represents measurement on a specimen which was just taken out of the potassium adsorption reactor, and the broken line represents the old specimens which were treated for potassium adsorption weeks ago. The change was found in the two ranges of the weight percent of potassium. The electrical conductivity increased in the low range, up to 2% potassium, except A1-3; and decreased in the high range, potassium from 2 to 7%. These preliminary results may suggest that the positive effect of intercalation compounds is dominant in the low range of potassium content and that the negative effects of microcracks and possibly a coating of potassium carbonate, are in the high range of potassium content.

G. Potassium Generator

In our early work, identical specimens placed in different locations in the reactor relative to the inlet of potassium-containing gas, absorbed different amounts of potassium under supposedly identical conditions. Such difficulty might be caused by the slow flow rate (or linear velocity) because of the reaction chamber being too large in its cross-section and the inability to cut off potassium-containing gas completely from the specimens during heating and cooling. An attempt was made to solve this problem by reducing the diameter of the reaction chamber to increase the linear velocity of potassium-argon gas mixtures and by using a by-pass tube between the potassium generator and absorption chamber.

The improved potassium generator and absorption chamber is shown in Fig. 51 and the mass balance of potassium for five kinds of coke specimens treated is shown in Fig. 52.

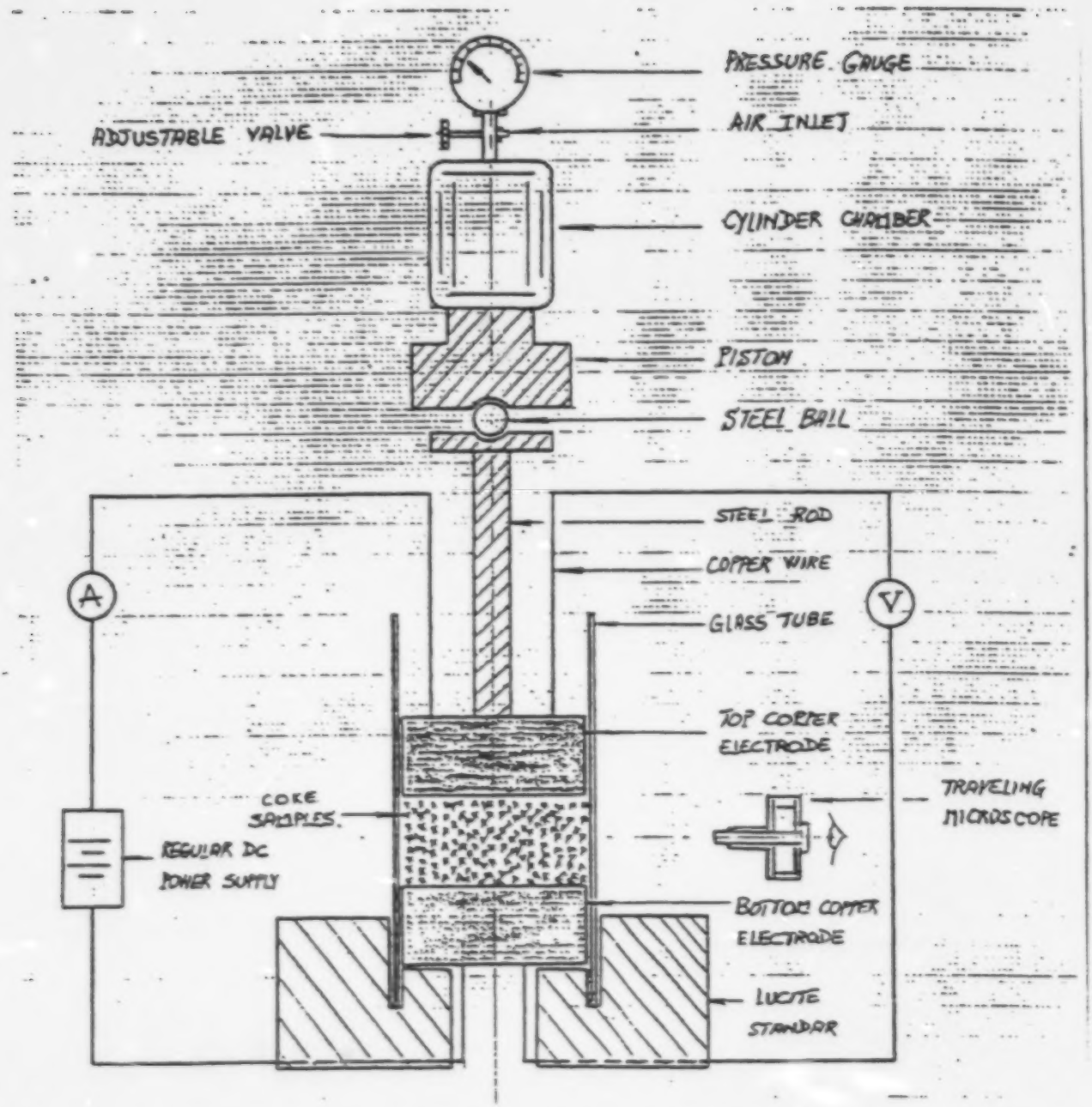


Fig. 42 Apparatus for the measurement of electrical conductivity.

Table 6 Calibration of pressure gauge with a Universal Flat Load Cell.

PRESSURE GAUGE	MICRO CELL (mV)						AVERAGE (mV)
	1	2	3	4	5	6	
0	0.331	0.331	0.331	0.329	0.331	0.331	0.331
5	0.066	0.058	0.055	0.067	0.064	0.076	0.064
10	-0.286	-0.263	-0.289	-0.269	-0.290	-0.271	-0.278
15	-0.630	-0.608	-0.637	-0.635	-0.644	-0.629	-0.631
20	-0.983	-0.968	-0.987	-0.983	-0.996	-0.980	-0.983
25	-1.331	-1.314	-1.341	-1.346	-1.346	-1.330	-1.335
30	-1.659	-1.667	-1.692	-1.672	-1.697	-1.678	-1.678
35	-2.039	-2.051	—	-2.047	—	—	-2.046

Table 7 Relationship between load applied and output of micro cell.

WEIGHT (KG)	MICRO CELL (mV)		AVERAGE (mV)
	1	2	
0	0.331	0.326	0.328
44	-0.242	-0.243	-0.242
88	-0.812	-0.815	-0.814
110	-1.098	-1.110	-1.104
132	-1.382	-1.390	-1.387
176	-1.950	-1.962	-1.956
220	-2.524	—	-2.524

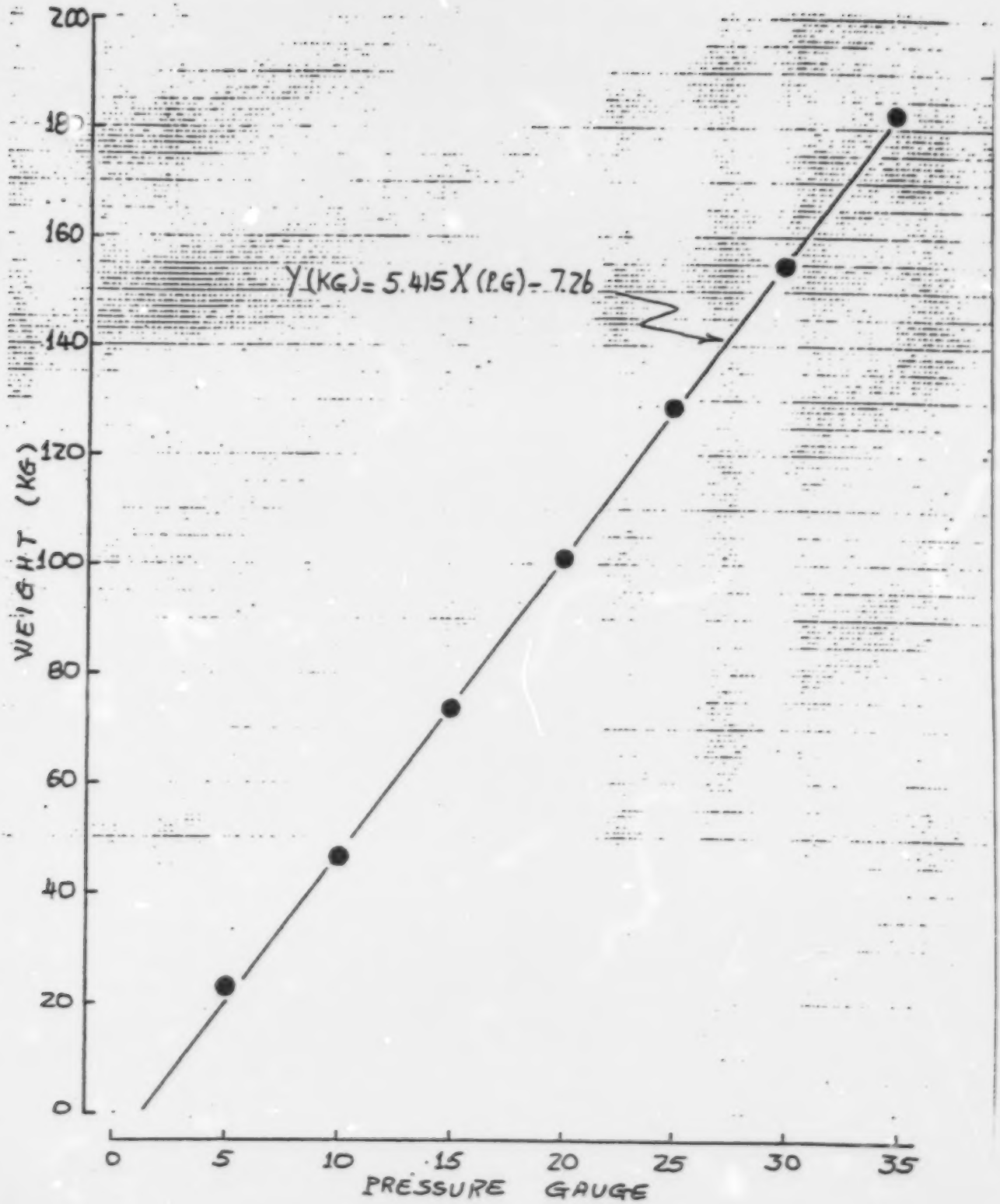


Fig. 43 Calibration line of pressure gauge.

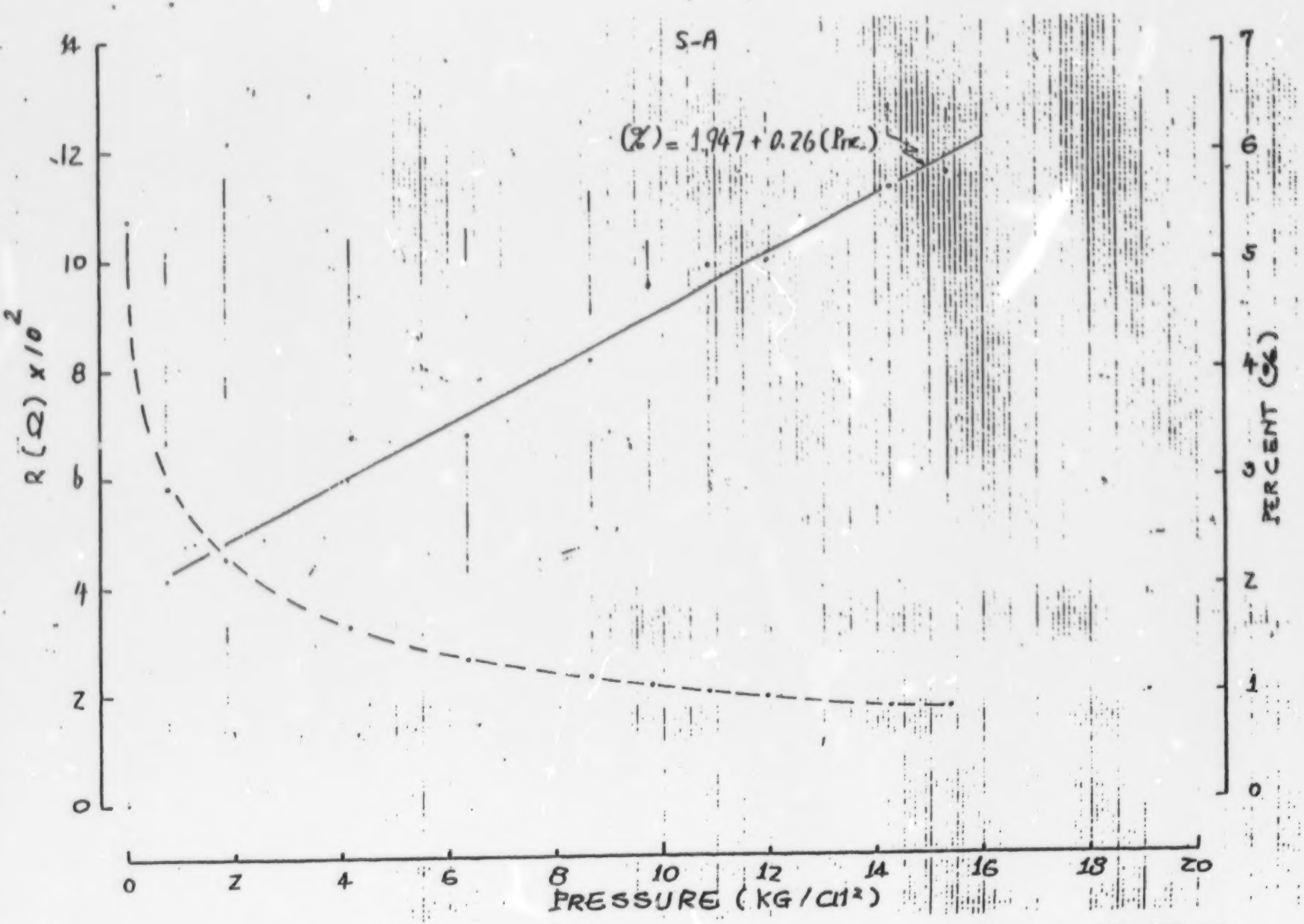


Fig. 44 Effect of pressure on the resistance of coke and the volume change (particle size 150 - 180 μm).

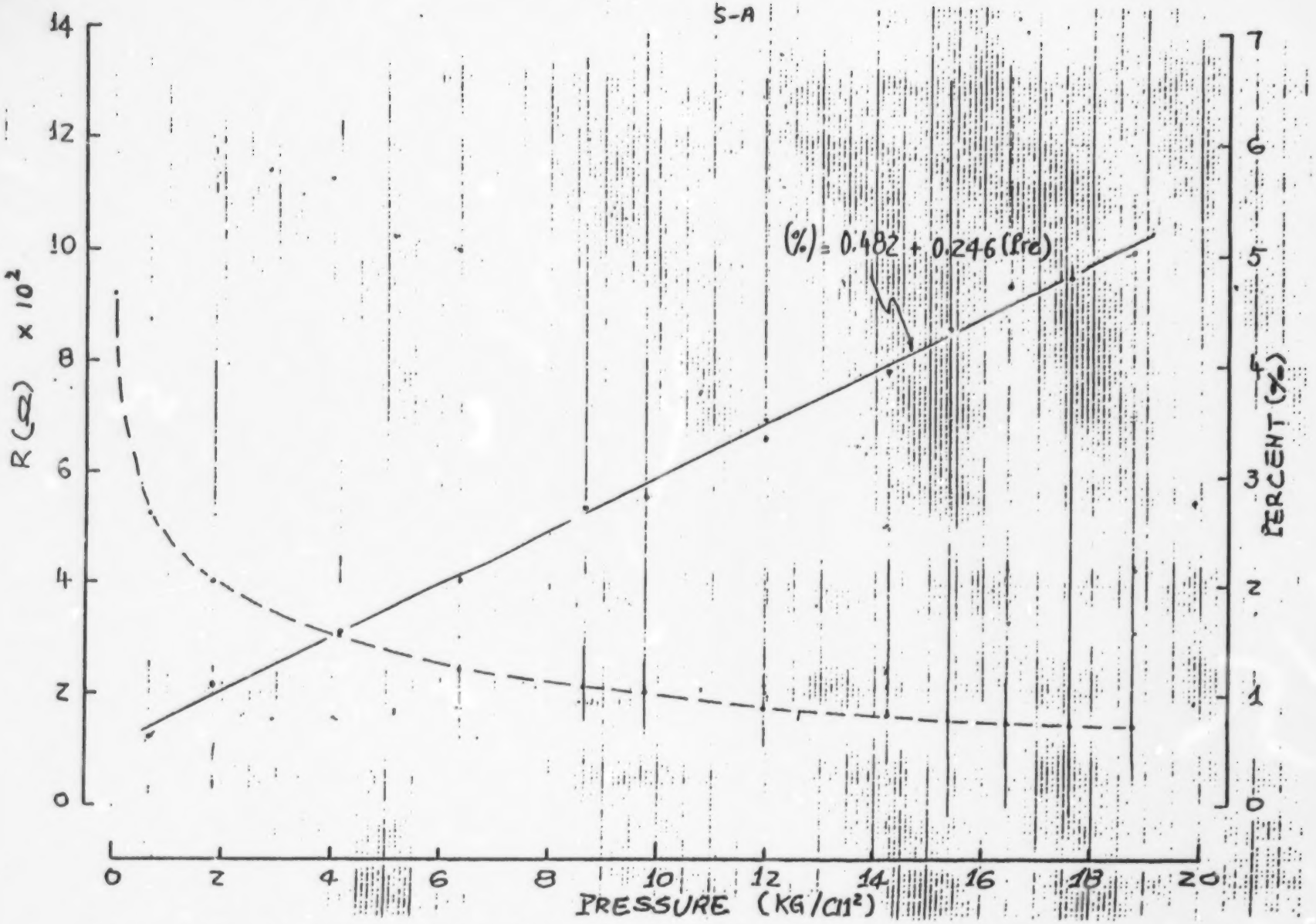


Fig. 45 Effect of pressure on the resistance of coke and the volume change (particle size 300 - 355 μm).

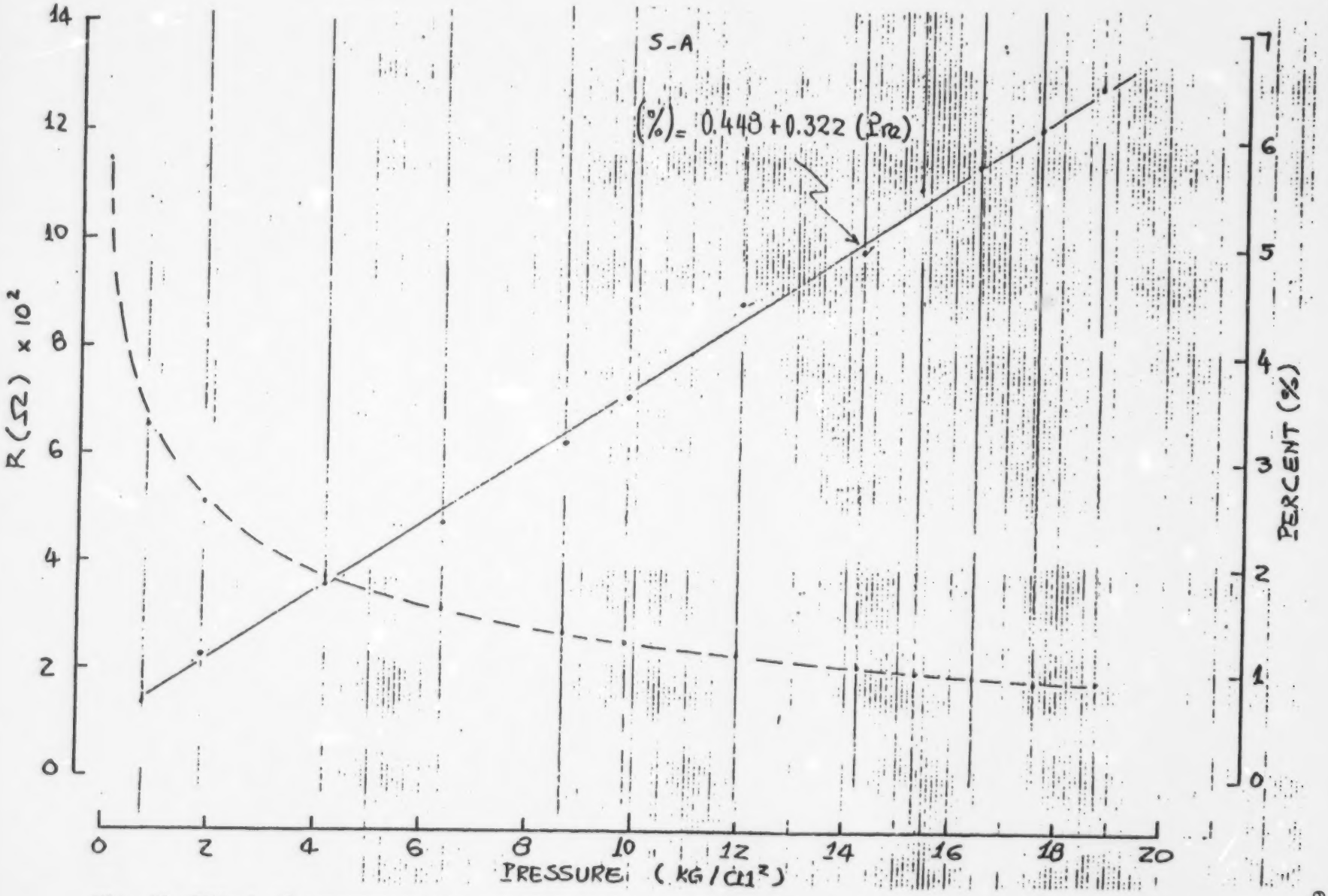


Fig. 46 Effect of pressure on the resistance of coke and the volume change (particle size 500 - 600 µm).

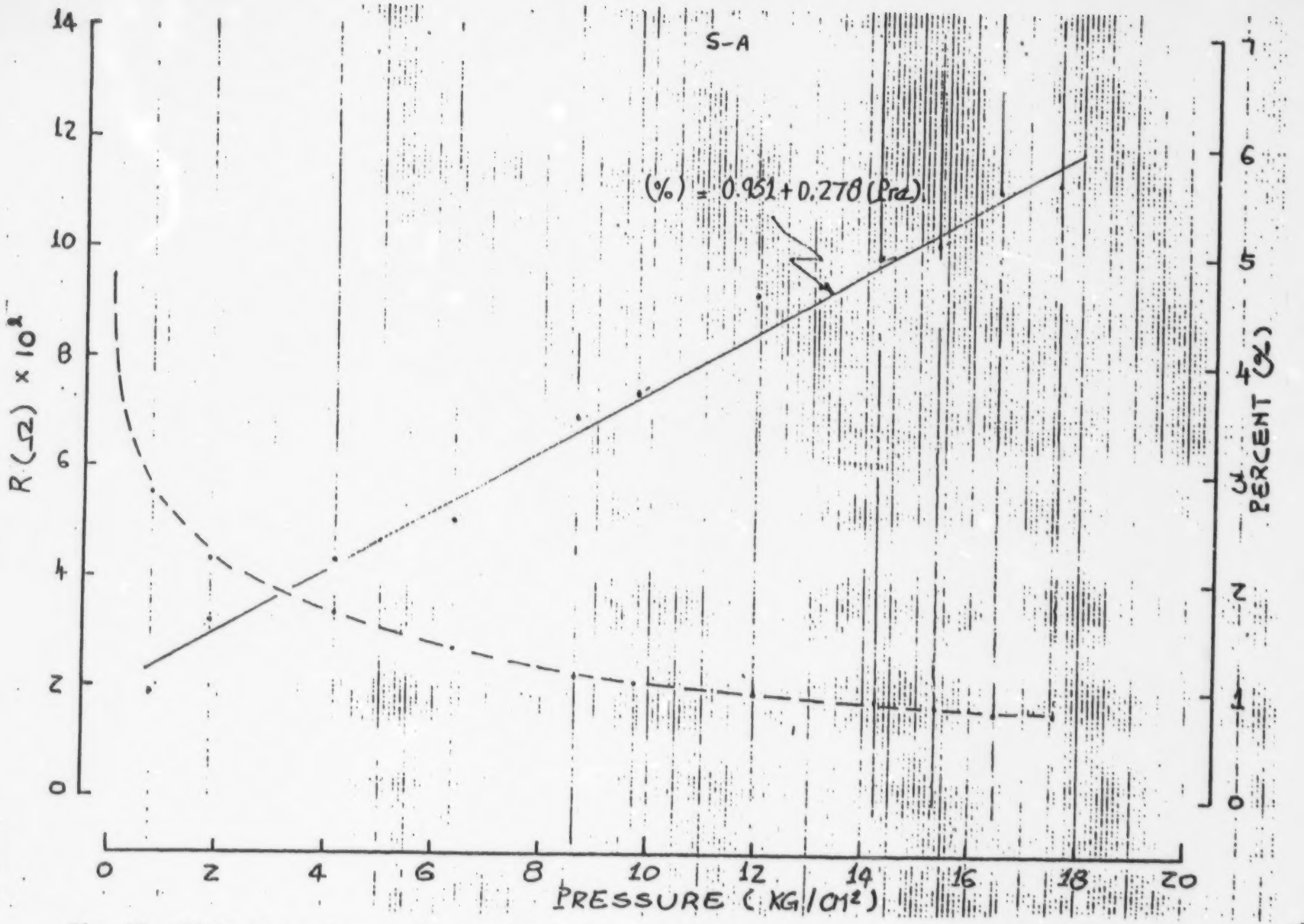


Fig. 47 Effect of pressure on the resistance of coke and the volume change (particle size 850 - 1000 μm).

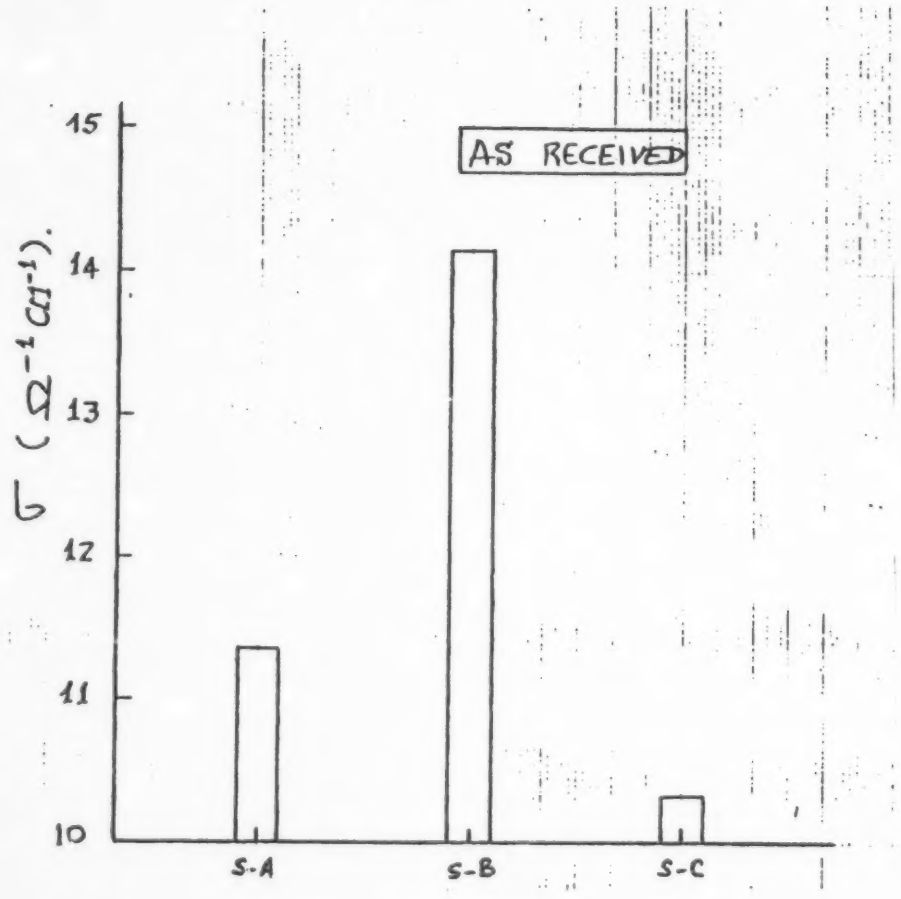


Fig. 48 Electrical conductivity of commercial cokes as received.

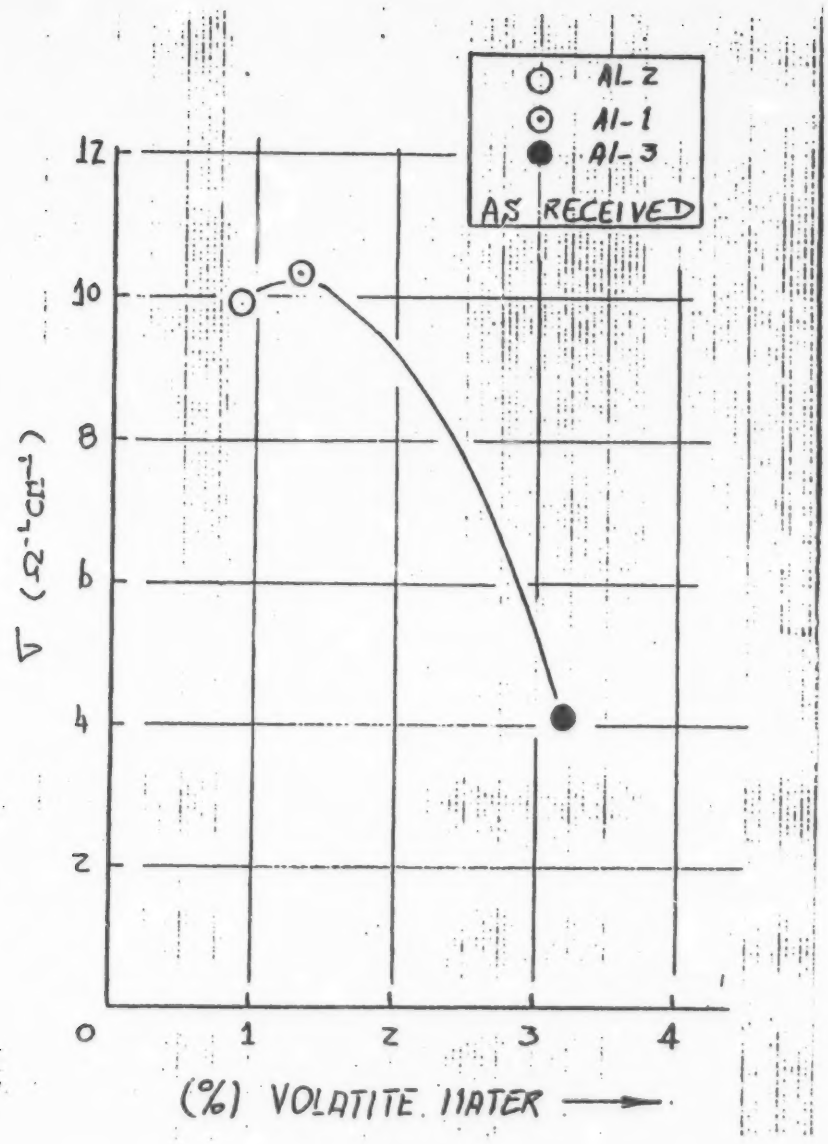


Fig. 49 The relation between electrical conductivity and volatile matter (%).

Table 8 Electrical conductivity $\sigma(\Omega^{-1}cm^{-1})$ after potassium adsorption.

(%)	SAMPLE	RECEIVING	NEW "K"	OLD "K"		
1.42	S-A	11.33	14.92 (+31.68)	8.8 (−22.33)		
2.26	S-B	14.14	5.12 (−63.79)	2.14 (−84.87)		
2.04	S-C	10.32	6.88 (−48.7)	5.92 (−42.63)		
0.36	Al-1	10.37	14.3 (+37.90)	K = 5 (%) 6.34 (−38.86)	K = 6.7 (%) 5.18 (−50.05)	
3.66	Al-2	9.92	4.24 (−57.26)	6.1 (%)	K = 7 (%) 4.43 (−55.34(%))	
1.21	Al-3	4.08	1.83 (−55.15)	5.7 (%)	K = 6.8 (%) 2.08 (−49.02)	
3.65	Rα	5.13	2.256 (−56.02)	4.4 (%) 2.69 (−47.56)	5.4 (%) 9.43 (+83.82)	6.7 (%) 8.50 (+65.70)

The values in parentheses are defined by $(\sigma - \sigma_o)\sigma_o \times 100$ where σ_o is the electrical conductivity as received and σ is the electrical conductivity after potassium adsorption.

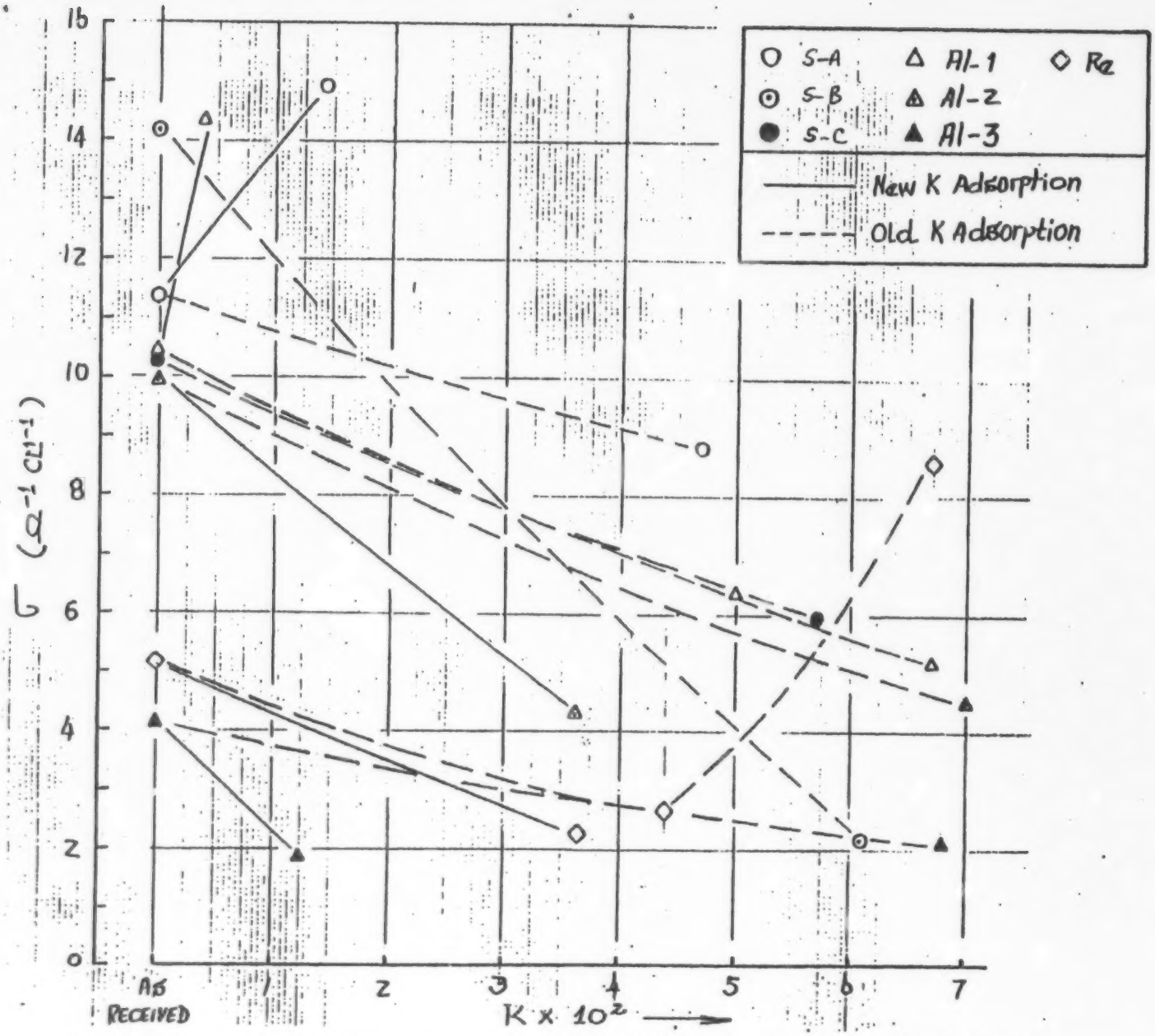


Fig. 50 The relation between electrical conductivity and potassium content in coke.

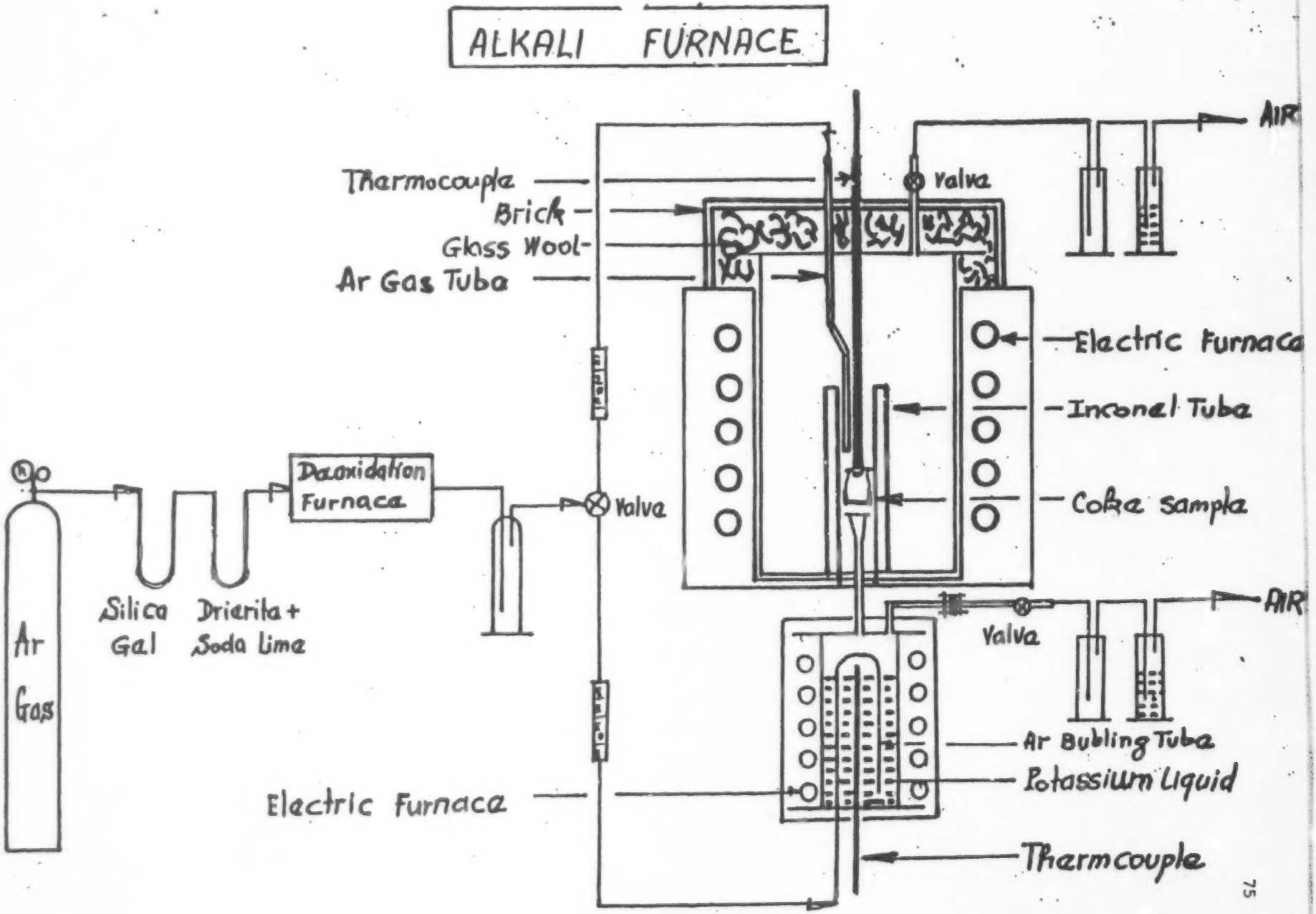


Fig. 51 Apparatus of potassium generator.

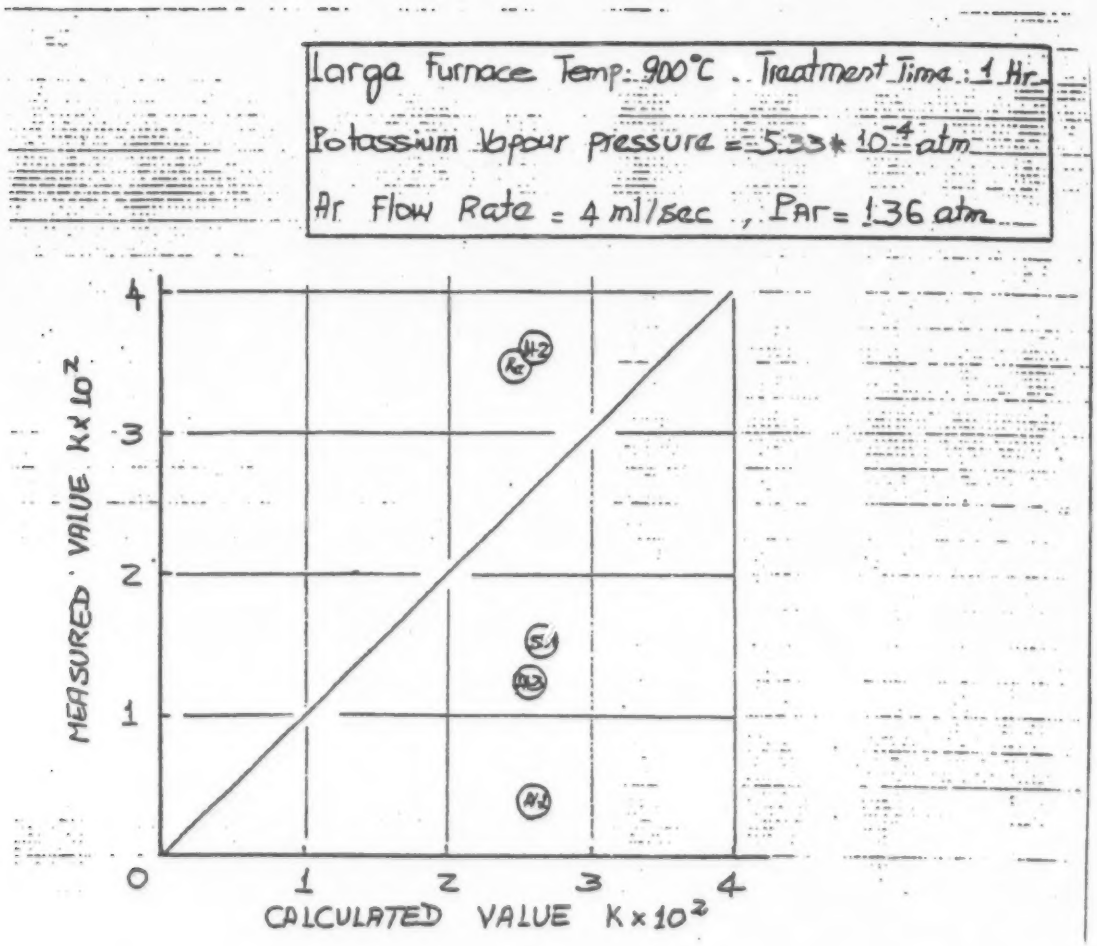

Large Furnace Temp: 900°C . Treatment Time : 1 Hr
Potassium Vapour pressure = 5.33 * 10⁻⁴ atm
Ar Flow Rate = 4 ml/sec , PAr = 1.36 atm
MEASURED VALUE K x 10²
CALCULATED VALUE K x 10²
0
1
2
3
4

Fig. 52 The relation between measured value and calculated value after improvement of the potassium generator.

10. CONCLUSIONS

A. The goal to relate reactivity and a measurable property of coke, instead of properties of coals in the blend and conditions of carbonization, has been substantially achieved. The property of coke under consideration is specific surface, particularly measured in terms of moisture absorption.

B. The technique of moisture absorption, which can be improved by using a hot water bath, is simple enough to be used by a worker in the quality control laboratory in a steel works.

C. The effect of potassium in tuyere samples on the reliability of moisture absorption technique is yet to be assessed.

D. The effects of potassium and hydrogen on the chemical reactivity (of fine particle) of coke are very pronounced.

11. FUTURE WORK

This [illegible]s aimed at generating knowledge so that chemical reactions involvin[illegible] in the stack and bosh of blast furnaces can be better understood. For the purpose of obtaining reproducible data, samples of fine particles were used.

In the steel industry, cokes are used in the form of large lumps to facilitate permeability in blast furnaces. Blast furnace men are more interested in the consequence of chemical reactions involving coke (i.e., degradation in strength and size), not in the physical chemistry of these reactions. The influence of chemical reactions on the mechanical properties of coke cannot be studied with powder specimens. The present work has provided the necessary background so that a study of practical importance can be initiated. Specimens of coke of a size ($\sim$ 20 mm in diamter) such that the gradient of degree of reaction from the surface to the center of the lump can be observed, will be used in our future work at McMaster University on changes in mechanical properties.

12. REFERENCES

(1) F.R.M. McDonnell, R.C. Pink and A.R. Ubbelohde, J. Chem. Soc., 1951, 191-197.

(2) D.M. Ottmers, H.G. Rase, I & EC Fundamentals, Vol. 5, No. 3, August, 1966, 302-310.

POOR

QUALITY

ORIGINAL